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發明 ~~新型~~ 專利說明書

一、發明 ~~新型~~ 名稱	中文	切斷式三層電池分離器
	英文	SHUTDOWN, TRILAYER BATTERY SEPARATOR
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經濟部中央標準局員工消費合作社印製

裝 訂 線

（由本局填寫）

承辦人代碼：
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本案已向：

美 國（地區） 申請專利，申請日期：1994.12.20案號：08/359,772，□有 □無主張優先權

有關微生物已寄存於：　　，寄存日期：　　，寄存號碼：

（請先閱讀背面之注意事項再填寫本頁各欄）

裝　訂　線

五、發明説明（ 1 ）

發明範圍

本發明指向一種切斷式電池分離器。

發明背景

切斷式電池分離器已爲人知悉。譬如參閱美國專利第4,650,730；4,731,304；5,240,655；5,281,491號；以及日本專利第6-20671號，每一上述之文件均納入本文供作參考。

在電池中，陽極及陰極由一分離器相互分離。今日之"鋰電池"非常普遍，因爲它們可產生高能量輸出。鋰電池市場可區分爲兩個部分："初級"鋰電池及"次級"鋰電池。初級鋰電池爲可丟棄式電池；而次級鋰電池爲可充電式電池。次級鋰電池有一難題在於其可能之短路，而此短路可使其自身出現快速之熱能散出。此種快速之熱能散出，會造成電池的爆炸。依此，使得切斷式電池分離器得以發展出來。

切斷式電池分離器概略地包含兩片聚合物材料之不同但並置之微孔隔膜。其中一種微孔隔膜係因其較低之熔點而選用，而另一種則因其相對之強度而選用。譬如，低熔點隔膜可爲聚乙烯材料而強度隔膜可爲聚丙烯材料。聚乙烯微孔隔膜具有大約130°-135℃之熔點，其已足夠低到只要在鋰電池中產生了短路，產生之熱能將會熔化聚乙烯且切斷或是塡充分離器的毛孔，因而阻止或禁止短路之可能發生。具有大約160℃之略高熔點之聚丙烯隔膜，可提供強度至分離器上，俾使其在產生短路時，保持分離器的完整性。

五、發明說明（ 2 ）

在美國國專利第4,650,730；4,731,304；5,240,655；及5,281,491號；以及日本專利第6-20671號中，發表了上述型式之切斷式電池分離器。在美國專利第4,650,730及4,731,304號的範例中，發表了厚度爲3-4 mils(1 mil爲千分之1吋)之雙層分離器。在日本專利第6-20671號中，發表一種具有大約1至2 mils厚度之切斷式雙層電池分離器。

在美國專利第5,240,655及5,281,491號中，發表多層式分離器。在美國專利第5,240,655號中之範例2及3，發表一種聚乙烯—乙烯丁烷共聚物—聚乙烯式之三層分離器。上述之每一分離器，均藉由共引伸、抽取、拉伸處理製得。

當設計新式之上述型式的切斷式電池分離器時，除切斷特徵外，另有幾個重要的因素。它們包含：薄度、穿刺強度以及剝離強度。在製造電池時，重要的是要有極薄的分離器，俾使通過分離器的電阻以及電池尺寸均可減小。良好之穿刺強度在電池製造中相當重要，尤其是製作"膠狀捲筒"式電池爲然，因爲陽極及陰極表面可粗糙到足以使得它們在製作過程中，穿破這些極薄之分離器。良好之剝離強度在電池製造中亦相當重要，因爲其可避免分離器之分層。依此，需要生產一種極薄之切斷式電池分離器，其具有足夠的穿刺強度及剝離強度以承擔嚴格的電池製造。

在次級鋰電池的製造中，良好的穿刺強度格外重要。用於次級鋰電池之陽極及陰極，基本上具有粗糙的表面。這些粗糙的表面，呈現特有之製造考量，因爲它們在電池裝配過程中會損壞薄片分離器。具有一切斷層及一強度層之

（請先閱讀背面之注意事項再填寫本頁）

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五、發明説明（3）

雙層式電池分離器，易於在製作過程中，被粗糙之電極表面損傷切斷層(其較強度層脆弱)。依此，需要一種電池分離器，其可特別地承擔在製作諸如次級鋰電池中所遭受到之粗糙側面電極。

發明總論

本發明指向於一種切斷式三層電池分離器。此分離器具有第一及一第三微孔隔膜，其間包夾一第二微孔隔膜。第一及第三隔膜較第二隔膜具有較大之穿刺強度；第二隔膜具有較低於第一或第三隔膜之熔化溫度。第一及第三隔膜最好用聚丙烯製作；第二隔膜最好用聚乙烯製作。

圖式簡述

爲了解釋本發明之故，圖式中顯示本發明各種之較佳方面；可是宜了解本發明並非限定在所示之精確排置及工具內。

圖1圖示一種三層式電池分離器，其可隨溫度(攝氏)改變而切斷一電池(由電阻歐姆來量測)。

圖2爲一種雙層化及三層成形結構之概示圖。

詳細説明

本發明藉由下面之詳細説明及非限定式範例而更詳細地加以描述。

此處所用之切斷式電池分離器，論及一種電池分離器，其在回應諸如熱能的快速放出之特定事件後，具有能力來切斷離子之移過分離器。在圖1中，一圓形説明切斷電池分離器的功能。切斷能力由電阻(歐姆)表示，而熱量的放出

由溫度(攝氏)表示。當溫度高過一初始範圍時，電阻沒有什麼變化，可是當溫度到達切斷層的熔化溫度時，電阻值突升。電阻突升後，電阻值將停滯不動，直到溫度到達強度層之熔化溫度。用來繪製圖1的數據，自一根據本發明製得之三層切斷式電池分離器中測試而得。此一三層式分離器，由聚丙烯(PP)—聚乙烯(PE)—聚丙烯(PP)製成。關於切斷式電池分離器的進一步資料，可自下面的文件中獲得：美國專利第4,640,730、第4,731,304、第5,2240,655、第5,281,491號、日本專利第6-20671號、1994年11月17日建檔、署名"製作交叉層微孔隔膜電池分離器之方法，及藉其製得之電池分離器"之美國專利申請第08/341,239號，以及1994年12月2日建檔、署名"切斷式雙層電池分離器"之美國專利申請第08/348,630號。以上每一專利文件均納入本文供作參考。

根據本發明之切斷式電池分離器，至少具有三層。當然，三層中之每一層均是呈微孔式，而最好其爲分開之微孔隔膜。(譬如參閱紐約州紐約市John Wiley & Sons公司出版之合成聚合物隔膜第二版(1985年)第7章第8.2節之Ibid，此一參考書納入本文供作參考)。最外層提供強度、尤其是對抗穿刺之強度，譬如粗糙的電極表面。此強度品質可以穿刺強度(稍後會有定義)來數量化。介於這些最外層之間的某一層，可提供切斷品質。最好是最外層的穿刺強度，較大於內切斷層，而內切斷層的熔化溫度，較低於最外強度層的溫度。在三層切斷式電池分離器的較佳實配例中，最

外強度層中包夾了內關斷層。

上面論及之最外層強度品質，爲層面之主要但非必需之唯一功能，其能力爲藉由提供較大的穿刺強度至分離器而便於電池的製造，同時可在短路發生時，保持分離器的整體性。最好是在鋰電池中，強度能力可藉由提供一種在大於或高於最低熔化電極(即指鋰材料)的溫度中將會熔化之材料來加以提供。此種材料之一範例爲聚石蠟，譬如：聚丙烯、或概略包含有聚丙烯之混合物、或聚丙烯的共聚物。

上面論及之內層切斷品質，爲層面之主要但非必需之唯一功能，其能力爲當短路發生時，關閉分離器的微孔。此基本上意謂切斷層將在某些溫度下熔化而掩蓋分離器的毛孔，因而藉由禁止離子的移過分離器而終止短路的產生。最好是在鋰電池中，切斷能力可藉由一種在至少低於最低熔化電極(即指鋰材料、鋰之熔點大約爲180℃)20℃之溫度下將會熔化之材料而提供。此種材料之一範例爲聚乙烯，或是概略地包含聚乙烯的混合物，或是概略地包含其熔化溫度高於110℃之聚乙烯共聚物。

這些分離器的厚度小於3 mils(每1 mil爲千分之一吋)(大約爲75微米)(1微米爲10^{-6}米)。這些分離器的厚度範圍最好在0.5 mils(大約12微米)及1.5 mils(大約爲39微米)之間。更佳的是分離器的厚度大約在1 mil(大約25微米)。分離器的總厚度爲個別層的總和。這些個別層最好具有大約相同的厚度。量測細節將稍後提出。

五、發明說明（6）

穿刺強度必須最好大於450克；而更佳之穿刺強度必須大於480克。這些量測值是以平均微孔數爲35%而得。量測細節將於稍後提出。

剝離強度必須最好大於或等於4克/吋(1克/公分)，更佳的是剝離強度必須大於或等於6克/吋(1.5克/公分)。量測細節將於稍後提出。

此一具創意分離器之製作過程，廣義地包含製作一第一及第三微孔隔膜，製作一第二微孔隔膜，以及將第一、第二及第三隔膜固合在一起。關於製作隔膜的較佳方法，其過程需要下列之步驟：引伸一聚合物而形成一薄片；退火該薄片；及拉伸退過火之薄片。製造這些薄片，尤其是聚乙烯或聚丙烯薄片之特定方法，將參照製造厚度超過1 mil之隔膜的方法討論。藉由非限定之範例，下列均置入本文供作參考之參考資料，說明製作厚度超過1 mil薄膜之技巧：美國專利第3,426,754；3,558,764；3,679,538；3,801,404；3,801,692；3,843,761；3,853,601；4,138,459；4,539,256；4,726,989以及4,994,335號，而上述之每一專利均置入本文供作參考。由於這些方法之知識是可想像的，因此製作薄膜之具創意過程，可藉由解釋介於以往技術之製作標準薄片(厚度大於1 mil)的方法及製作薄膜(厚度小於大約1/2 mil)之具創意方法間的差異而於稍後加以說明。

下面所討論之關於引伸、退火及拉伸間的差異，係基於一種配具70 mil心軸間隙之27吋模具形狀。如果模具外形改變，則差異隨之改變。譬如，如果使用6吋模具，介於標

準膜片處理及薄膜片處理間之模具溫度差別甚小。如果不顧模具外形，薄膜片將需較少之淬火空氣。

關於引伸條件，標準膜片處理基本上較薄膜片處理需要較強之淬火空氣條件以及較低之引伸溫度。譬如，標準膜片處理之適當淬火條件，包含：大約6吋水柱高之空氣壓力；在10/64至15/64吋範圍內之空氣環間隙；以及1至2吋高的空氣環；但在另一方面，薄膜片處理之適當淬火條件，包含：大約0.6至3吋水柱高之空氣壓力；在5/64至10/64吋範圍內之空氣環間隙；以及大約1至2吋高之空氣環。標準膜片處理(譬如使用Exxon's Escorene聚丙烯4292型樹脂)之適當引伸條件，包含：191至198℃範圍內之模具溫度，以及200至205℃的外筒溫度；但在另一方面，薄膜片處理(使用相同材料)之適當引伸條件，包含：210℃(針對0.5 mil厚度的最終產品)至224℃(針對0.33 mil厚度最終產品)範圍內之模具溫度，以及210℃之外筒溫度。

關於退火及拉伸條件，層面間的黏合(以剝離強度量測)必須低於標準式處理，俾使個別層在它們被分層時，不致於分開(即撕開)。阻抗分開之能力，正比於層面的厚度。因此，如果層面固合在一起(由於黏合力)且固合力大於分割阻抗時，層面不經分割是不會分開的(分層)。譬如，具有大約1 mil(1 mil爲千分之一吋)厚度的層面黏合力，必須低於大約15克/吋；而針對0.5 mil厚度的層面而言，黏合力必須低於大約8克/吋；而對一0.33 mil厚度的層面，黏合力必須低於5克/吋。爲了降低黏合值，本具創意處理之退火/

五、發明説明（8）

拉伸溫度，小於標準式處理時的溫度。譬如，一種聚丙烯薄片的退火/拉伸溫度範圍爲120-125℃(具創意處理)，而標準式處理之溫度範圍爲140-150℃，而對聚乙烯薄片而言，大約是110℃(具創意處理)相對於115℃(標準式處理)。

爲了避免回縮變形，整平之兩層式薄片被加以操作，直到三層式分離器得以成形方止。薄片之分層外形如圖2所示。在圖2中，顯示一分層及三層型式結構10。此結構10包含一底面佈置圖12及一上面佈置圖14。佈置圖12及14是相同的，但爲了正視圖之故(可有效地使用空間)，因此僅詳細地討論佈置圖12。佈置圖12中包含三個未纏繞之工作站16、18及20。工作站16及20支撐聚丙烯微孔隔膜之捲材(即單捲一雙層)，而工作站18支撐聚乙烯微孔隔膜之捲材(即單捲一雙層)。單層型式的隔膜(即或爲聚丙烯隔膜、或爲聚乙烯隔膜)，薄度大約爲1/3 mil，此種厚度的隔膜或薄片，傾向於回縮或皺摺。爲了避免回縮及皺摺，這些隔膜經處理(儘可能地)而成雙層型式(大約2/3 mil厚)。聚丙烯薄片24及聚乙烯薄片26自它們之滾輪中鬆開，分層—某些狀況下需要導輪22的協助，接著重新結合而形成三層式母質28。自結構10中，4組三層式母質28成形。最好至少有4組三層式母質，俾可避免回縮問題及更有效地使用裝備(經濟性理由)。對處理之經濟性言之，最好是最低量之至少兩組三層式母質。母質28被推前至固合站30。

關於固合隔膜在一起之較佳方法，數種固合方法受到期盼。廣言之，固合方法包含研光，以黏劑黏合及焊合。黏

劑之應用可包含之空氣微粒化；雕刻/篩選印刷；液壓噴塗；以及超音波噴塗。黏劑之選擇及黏劑施用率必須加以選定，俾使分離器的多孔性不會有不利的影響。焊合技術包含熱焊合及超音波焊合。焊合過程及焊合類型之能量大小，必須加以選定，俾使分離器的多孔性，更沒有不利的影響。最好是固合係藉由砑光完成，其在125至130℃的溫度範圍及此溫度下之大約2至10分鐘的駐留時間而被夾合。

固合後，三層切斷式電池分離器被重新纏繞而使用於電池的製作，尤其是次級鋰電池已在技術上廣被周知。

關於上述發明之進一步資料，可自下面的非限定式範例中獲得。其中所涉及之測試方法，將於下面提出。

測試方法

Gurley值：根據ASTM-D726(B)規範測試

Gurley值係藉由Gurley密度計（即4120型）量測之對氣流的阻抗。Gurley值是在12.2吋水柱高之壓力下，將10 cc的水通過一平方吋產品面積所需之時間秒。

厚度：依據T4110m-83規範，此方法係由紙漿及紙品工業技術協會主辦下發展出來。厚度的決定，係使用配具1/2吋直徑之圓形鞋樣的精密測微尺，其以7 psi的壓力接觸樣本。橫過樣品寬度而取得之10次個別測微尺讀數之平均數定爲厚度尺寸。

多孔性： 根據ASTM D-2873規範。

密度：根據ASTM D-792規範。

穿刺強度：越過拉伸產品寬度方向而得之10次量測值並求其平均數。一種Mitech Stevens產製之LFRA結構分析儀被加以使用。針頭直徑爲1.65毫米，其矢徑爲0.5毫米。下降率爲2毫米/秒，而偏折率爲6毫米。薄片被緊固在夾持裝置上，其中央孔爲11.3毫米。經針頭刺穿之薄片的位移數(以毫米爲單位)，係針對由測試薄片所產生之阻力(單位爲克力)而記錄得之。最大之阻力值即爲穿刺強度。

剝離強度：剝離強度係使用張力及壓縮力測試器而量測，用以決定需用多少克的力來分開兩片固合隔膜之1吋寬部位。剝離率爲6吋/分鐘。3個量測值經由越過織布而得且求取其平均值。

熔化指數：根據ASTM D1238規範；聚乙烯爲190℃/2.16公斤；聚丙烯爲230℃/2.16公斤。

範例

上面發表過之切斷式三層電池分離器，以下面之方式製得：

其所使用之聚丙烯及聚乙烯樹脂，在表1及2中提出：

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五、發明說明（ 11 ）

表 1

聚丙烯(PP單聚合體)

	樹脂	密度 (克/公分^3)	熔化指數 (克/10分鐘)	供應商
A	Escorene PP4292	0.90	1.4	Exxon化學公司
B	Fina PP 3271	0.905	1.5	Fina油脂及化學公司
C	Fina PP 3281	0.905	1.1	Fina油脂及化學公司
D	Escorene PP4292 (成核形)	0.90	1.4	Exxon化學公司
E	Escorene PP4372*	0.90	1.4	Exxon化學公司
F	Escorene PP3182	0.90	3.0	Exxon化學公司

*：含有一種抗阻劑

表 2

聚乙烯(高密度PE)

	樹脂	密度 (克/公分^3)	熔化指數 (克/10分鐘)	供應商
G	Fina HDPE GF7750	0.958	0.70	Fina油脂及化學公司
H	Escorene HDZ107	0.964	0.30	Exxon化學公司

引伸器裝置之外形如表3所示：

表 3

引伸器

	長/寬比	外筒尺寸	模具尺寸	模具開口	地面長度	放大率
E1	24	2.5吋	12吋或27吋	70 mil	3吋	1
E2	24	3.5吋	12吋或27吋	70 mil	3吋	1
E3	30	1.25吋	6吋	70 mil	3吋	1

樹脂如表4所提地被加以引伸，俾如表4所示地構成一圓形母質薄片(中空管形)：

表4

引伸條件

產品	樹脂(見表1及2)	引伸器/模具尺寸(見表3)	引伸器溫度(℃)	熔化溫度(℃)	模具溫度(℃)	氣環高度(吋)	淬火空氣壓縮(吋，水柱高)	氣環開口(吋)	厚度(mil)	線性速率(呎/分鐘)
P1	A	E3/6吋	200	205	205	1吋	1.5吋	0.078吋	0.38	42
P2	C	E3/6吋	205	215	215	1吋	1.5吋	0.078吋	0.38	42
P3	C	E2/27吋	230	243	243	1吋	1.2吋	0.078吋	0.38	47
P4	A	E2/27吋	210	224	224	1吋	1.2吋	0.078吋	0.38	50
P5	A	E2/12吋	220	224	224	1吋	1.2吋	0.078吋	0.38	50
P6	B	E2/27吋	210	224	224	1吋	1.2吋	0.078吋	0.38	50
E1	G	E1/27吋	200	220	200	1吋	1.0吋	0.078吋	0.38	60
E2	H	E1/12吋	180	199	185	1.25吋	1.0吋	0.094吋	0.59	60

母質薄片在一8層薄片中退火。此意謂由於母質薄片如漲氣管般引伸，當它們被壓陷時，它們產生兩層薄片。四組這些雙層薄片被捲繞在一起而形成8層式薄片。退火條件在下面表5中提出：

表 5

退火條件

產品(見表4)	退火溫度	退火時間，分鐘	剝離強度(克/吋)
P1	136	16	-
P2	140	16	-
P3	120	16	-
P4，P5	120	16	2
P6	135	16	0
E1	110	19	1
E2	115	19	1

退火後之母質薄片被拉伸而構成微孔隔膜。退火過之母質薄片被拉伸爲16層薄片(來自一引伸管形母質之8捲2層式薄片)。退過火之母質薄片，可變通地拉伸成8層式薄片或24層式薄片。拉伸條件在表6中提出：

表 6

拉伸條件

產品(見表5)	冷拉溫度(℃)	冷拉*	熱拉溫度(℃)	熱拉*	熱鬆弛溫度(℃)	熱鬆弛*，1	厚度	Gurley值(秒)
P4，P5	外界溫度	25%	120℃	115%	120℃	40%	0.33	12
P6	外界溫度	25%	135℃	115%	135℃	40%	0.33	10
E1	外界溫度	40%	110℃	110%	110℃	50%	0.33	8
E2	外界溫度	45%	115℃	105%	115℃	40%	0.5	11

*：拉伸/鬆弛百分比係基於冷拉伸前之最初長度。

1：鬆弛步驟表示容許拉伸過之薄片的回縮。

譬如16層薄片之微孔隔膜，被分層爲兩層薄片。兩層薄片的邊緣部位被剪修，因而將兩層薄片分開成個別之分開層。聚丙烯層被剪修成較聚乙烯層寬0.5吋。

三層式母質由砑光法以128℃之溫度固合在一起，其線性速率爲25呎/分鐘，而在固合溫度下之駐留時間爲5-10分鐘。

根據前述範例所製作之三層式分離器，具有表7所提出之特性：

表7

三層式分離器特性

產品	PP/PE/PP (見表6)	厚度(mil)	Gurley值 (秒)	穿刺強度 (克)	黏合力 (克/公分)
T1	P2/E1/P2	1.02	20	480	4.3
T2	P4,P5/E1/P4,P5	1.01	29	480	-
T3	P6/E1/P6	1.01	22	483	-
T4	P4,P5/E2/P4,P5	1.15	30	500	6.5

三層式電池分離器之特性，在表8中與其他之電池分離器比較：(Celgard® 型單層式聚丙烯；Celgard® 型單層式聚乙烯；雙層式聚丙烯/聚乙烯(見1994年12月2日建檔之美國第08/348,630號專利申請)；以及交叉層聚乙烯(見1994年11月11日建檔之美國第08/341,239號專利申請))：

五、發明說明（15）

表 8

三層式(PP/PE/PP)(PP：聚丙烯；PE：聚乙烯)與其他電池分離器之比較

特性	單層式PP	單層式PE	雙層式 PP/PE	交叉層 PP/PE	三層式 PP/PE/PP
厚度(mil)	1.0	1.0	1.0	1.0	1.0
多孔性(%)	38	38	38	38	38
Gurley值(秒)	25	25	25	25	25
關斷溫度(℃)	165	132	132	132	132
關斷溫度範圍(℃)	-	20	35	20	35
穿刺強度(克)	380	290	490(PP) 300(PE)	490	480

本發明在不偏離其精神或主要特質下，可實體化爲其他特定之型式，因而在說明本發明範圍之上述規格外，必須另外參考增附之申請專利範圍。

（請先閱讀背面之注意事項再填寫本頁）

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四、中文發明摘要（發明之名稱：切斷式三層電池分離器　　　　　　　　　　　　）

本發明係指一種切斷式三層電池分離器，此分離器具有第一及第三微孔隔膜，其間包夾一第二微孔隔膜。第一及第三隔膜較第二隔膜具有較大之穿刺強度；第二隔膜具有較低於第一或第三隔膜之熔化溫度。

英文發明摘要（發明之名稱：SHUTDOWN, TRILAYER BATTERY
SEPARATOR　　　　　　　　　　　　）

The present invention is directed to a shutdown, trilayer battery separator. The separator has a first and a third microporous membranes sandwiching a second microporous membrane. The first and the third membranes have a greater puncture strength than the second membrane. The second membrane has a lower melting temperature than either the first or the third membranes.

（請先閱讀背面之注意事項再填寫本頁各欄）

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六、申請專利範圍

1. 一種切斷式三層電池分離器，包含一第一及一第三微孔聚丙烯隔膜，而其中間包夾一微孔聚乙烯隔膜。
2. 根據申請專利範圍第1項之電池分離器，其另包含一自大約0.5至大約1.5 mils(每1 mil爲千分之一吋)範圍內之厚度。
3. 根據申請專利範圍第2項之電池分離器，其另包含一大約爲1 mil之厚度。
4. 根據申請專利範圍第1項之電池分離器，其中該穿刺強度大於或等於大約450克。
5. 根據申請專利範圍第4項之電池分離器，其中該穿刺強度大於或等於480克。
6. 根據申請專利範圍第1項之電池分離器，其另包含一大於或等於每吋4克之剝離強度。
7. 根據申請專利範圍第6項之電池分離器，其中該剝離強度大於或等於每吋6克。
8. 一種電池，包含根據申請專利範圍第1項之分離器。
9. 一種切斷式電池分離器，包含一第一及一第三微孔聚丙烯隔膜，其間包夾一微孔聚乙烯隔膜；該分離器具有：一大約0.5 mils至大約1.5 mils範圍內之厚度；一大於或等於大約450克之穿刺強度；以及一大於每吋4克之剝離強度。
10. 根據申請專利範圍第9項之關斷式分離器，其中該厚度爲大約1 mil。
11. 根據申請專利範圍第9項之關斷式分離器，其中該穿刺

六、申請專利範圍

強度大於或等於大約480克。

12. 根據申請專利範圍第9項之關斷式分離器，其中該剝離強度大於或等於大約每吋6克。

13. 一種電池，包含根據申請專利範圍第9項之電池。

14. 一種方法，用以製作一微孔隔膜，隔膜具有一小於大約0.5 mils之厚度，該方法包含以下步驟：

引伸一中空管；

將中空管本身壓陷而構成包含兩層式之平滑薄片；

退火平滑薄片；

拉伸平滑薄片；及

捲纏平滑薄片，其介於兩層面間之黏合力小於每吋8克。

15. 根據申請專利範圍第14項之製作微孔隔膜方法，隔膜具有一小於或等於大約0.33 mils之厚度，其中之黏合力小於每吋5克。

16. 根據申請專利範圍第14項之方法，其另包含淬火已引伸中空管步驟，其配具之氣體具有之空氣壓力範圍係自0.6至3.0吋之水柱高度。

17. 一種方法，用以製作一三層切斷式電池分離器，其包含之步驟有：

提供一第一及第三平面薄片，其包含兩層根據申請專利範圍第14項之方法所製之微孔聚丙烯隔膜；

提供一第二平面薄片，其包含兩層根據申請專利範圍第14項之方法所製成之微孔聚乙烯隔膜；

六、申請專利範圍

分層第一及第三微孔聚丙烯隔膜之平面薄片；

分層第二聚乙烯微孔隔膜之平面薄片；

重新層合個別層面而構成一聚丙烯—聚乙烯—聚丙烯結構；

固合結構體以構成三層式分離器；及

捲繞分離器。

18. 根據申請專利範圍第17項之方法，其中之固合包含研光或以黏劑或焊接法黏合。

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ABSTRACT

The present invention is directed to a shutdown, trilayer battery separator. The separator has a first and a third microporous membranes sandwiching a second microporous membrane. The first and the third membranes have a greater puncture strength than the second membrane. The second membrane has a lower melting temperature than either the first or the third membranes.

Shutdown, Trilayer Battery Separator

Field of the Invention

The present invention is directed to a shutdown battery separator.

Background of the Invention

Shutdown battery separators are known. For example, see U.S. Patent Nos. 4,650,730; 4,731,304; 5,240,655; 5,281,491; and Japanese Kokai No. 6-20671, each of the foregoing is incorporated herein by reference.

In batteries, the anode and cathode are separated from one another by a separator. Today, "lithium batteries" are very popular because they are able to generate high energy outputs. The lithium battery market can be divided into two groups, the "primary" lithium battery and the "secondary" lithium battery. The primary lithium battery is a disposable battery, while the secondary lithium battery is a rechargeable battery. A problem associated with secondary lithium batteries is its potential for short circuiting. This short circuit may manifest itself with a rapid evolution of heat. This rapid evolution of heat can cause the battery to explode. Accordingly, the shutdown battery separator was developed.

The shutdown battery separator generally comprises two polymerically dissimilar and juxtaposed microporous membranes. One microporous membrane is chosen for its relatively low melting point and the other for its relative strength. For example, the low melting point membrane may be a polyethylene material and the strength membrane may be a polypropylene material. The polyethylene microporous membrane has a melting point of approximately 130° - 135°C which is sufficiently low that in the event of a short circuit in a lithium battery, the heat generated will melt the polyethylene and shutdown, or fill in the pores of the separator, and thereby stop or inhibit the likelihood of a short circuit. The polypropylene membrane which has a substantially higher melting point, approximately 160°C, provides strength to the separator so that it maintains the separator's integrity in the event of a short circuit.

In U.S. Patent Nos. 4,650,730; 4,731,304; 5,240,655; and 5,281,491, and Japanese Kokai 6-20671, shutdown battery separators of the foregoing type are disclosed. In the examples of U. S. Patent Nos. 4,650,730 and 4,731,304, bilayer separator thicknesses of 3-4 mils are disclosed. In Japanese Kokai 6-20671, a shutdown, bilayer battery separator has a thickness of about 1 to 2 mils.

In U.S. Patent Nos. 5,240,655 and 5,281,491, multi-ply separators are disclosed. In Examples 2 and 3 of U.S. Patent No. 5,240,655, a polyethylene - ethylene butene copolymer - polyethylene trilayer separator is disclosed. In Example 4 of U.S. Patent No. 5,281,491, a polyethylene - ethylene butene copolymer - polyethylene trilayer separator is disclosed. Each of the foregoing separators is made by a coextrustion, extraction, stretching process.

When designing new shutdown battery separators of the foregoing type, several factors, in addition to the shutdown characteristics, are important. They include: thinness, puncture strength, and peel strength. In the manufacture of batteries, it is important to have extremely thin separators, so that the electrical resistance across the separator, as well as, the size of the battery, may be reduced. Good puncture strength is important in battery manufacture, particularly in the manufacture of "jelly roll" type batteries because the surfaces of the anode and the cathode can be sufficiently rough that they can puncture these extremely thin separators during manufacture. Good peel strength is important in battery manufacture because it prevents delamination of the separator. Accordingly, there is a need to produce an extremely thin, shutdown battery separator that has a sufficient puncture strength and peel strength to withstand the rigors of battery manufacture.

In the manufacture of secondary lithium batteries good puncture strength is of particular importance. The anode and cathode used in secondary lithium batteries typically have rough surfaces. These rough surfaces present a special manufacturing consideration because they can damage the thin separators during the battery assembly. Bilayer battery separators, that have a shutdown layer and a strength layer, are suspectable to damage of the shutdown layer (it is weaker than the strength layer) during manufacture, by the rough electrode surface. Accordingly, there is a need for a battery separator that can withstand, among other things, the rough sided electrodes encountered in the manufacture batteries, for example, secondary lithium batteries.

Summary of the Invention

The present invention is directed to a shutdown, trilayer battery separator. The separator has a first and a third microporous membranes sandwiching a second microporous membrane. The first and the third membranes have a greater puncture strength than the second membrane. The second membrane has a lower melting temperature than either the first or the third membranes. The first and the third membranes are preferably made from polypropylene. The second membrane is preferably made from polyethylene.

Description of the Drawings

For the purpose of explaining the invention, there is shown in the drawings various preferred aspects of the invention; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown.

Fig. 1 is a graphical representation of a trilayer battery separator's ability to shutdown a battery (as measured by electrical resistance, in ohms) as a function of temperature (in °C).

Fig. 2 is a schematic illustration of a deplying and trilayer formation set-up.

Description of the Invention

The present invention shall be described in further detail below by way of the following detailed description and the non-limiting examples.

Shutdown battery separator, as used herein, refers to a battery separator that has the ability to shutdown ion migration across the separator in response to a particular event, for example, the rapid evolution of heat. In Figure 1, a graph illustrates the function of a shutdown battery separator.

Shutdown ability is represented by resistance (in ohms), and the evolution of heat is represented by temperature (in°C). As the temperature increases over an initial range, resistance is little changed. Resistance values spike-up, however, as the temperature reaches the melt temperature of the shutdown layer. After the resistance spike-up, the resistance values plateau until the temperature reaches the melt temperature of the strength layers. The data used for plotting the graph of Figure 1 was obtained from tests on a trilayer shutdown battery separator, made according to the instant invention. This trilayer separator was constructed from polypropylene (PP) - polyethylene (PE) - polypropylene (PP). Further information about shutdown battery separators maybe obtained from U.S. Patent Nos. 4,640,730; 4,731,304; 5,2240,655; 5,281,491; Japanese Kokai No. 6-20671; U.S. Patent application No. 08/341,239 filed November 17, 1994, entitled "Methods of Making Cross-Ply Microporous Membrane Battery Separators, and the Battery Separators Made Thereby"; and U. S. Patent application No. 08/348,630 filed December 2, 1994, entitled "Shutdown, Bilayer Battery Separator", each of which is incorporated herein by reference.

The shutdown battery separators according to the instant invention has at least three layers. Each of these layers is, of course, microporous, and preferably, it is a discrete microporous membrane. (For example see Kesting, R.E., Synthetic Polymeric Membranes, 2nd Ed., John Wiley & Sons, New York City, NY, (1985) at section 8.2 versus Ibid., Chapter 7, this reference is incorporated herein by reference.) The outermost layers provide the strength, particularly strength to resist puncture, for example by rough electrode surfaces. This strength quality maybe quantified as puncture strength (defined hereinbelow). A layer between those outermost layers provides the shutdown quality. Preferably, the puncture strength of the outermost layers is relatively greater than that of the inner shutdown layer, and the melting temperature of the inner shutdown layer is relatively less than that of the outermost strength layers. In the preferred embodiment of the trilayer, shutdown battery separator, the outermost strength layers sandwich the inner shutdown layer.

The strength quality of the outermost layers referred to above is the principal, but not necessarily the sole, function of the layer which is the ability to facilitate the manufacture of the battery by providing greater puncture strength to the separator, as well as, to maintain the integrity of the separator in the event of a short circuit. Preferably, in lithium batteries, the strength capabilities can be provided by a material that will melt at a temperature at about or greater than the melting temperature of the lowest melting electrode (e.g., the lithium material). An example of such a material is a polyolefin, for example: polypropylene or a blend comprising substantially polypropylene or copolymer of polypropylene.

The shutdown quality of the inner layer referred to above is the principal, but not necessarily the sole, function of the layer which is the ability to close the micropores of the separators in the event of a short circuit. This typically means that the shutdown layer will melt, at some temperature, blind the pores of the separator, and thereby terminate the short circuit by prohibiting ion migration across the separator. Preferably, in lithium batteries, the shutdown capabilities can be provided by a material that will melt at a temperature at least 20°C below the melting temperature of the lowest melting electrode (e.g., the lithium material, the melting point of lithium is about 180°C). An example of such a material is polyethylene or a blend comprising substantially polyethylene or a copolymer comprising substantially polyethylene with melting temperature greater than 110°C.

The thickness of these separators is less than 3 mils (about 75 microns). These separators preferably range in thickness between 0.5 mil (about 12 microns) and 1.5 mils (about 38 microns). Most preferably, the separator has a thickness of about 1 mil (about 25 microns). The total thickness of the separator is predominantly the sum of the individual layers. These individual layers, preferably, have about equal thickness. Measurement details are set forth below.

The puncture strength should preferably be greater than 450 grams. Most preferably the puncture strength should be greater than 480 grams. These measurements are made at an average porosity of 35%. Measurement details are set forth below.

The peel strength should preferably be greater than or equal to 4 grams/inch (1 gram/centimeter). Most preferably, the peel strength should be greater than or equal to 6 grams/inch (1.5 gram/centimeter). Measurement details are set forth below.

The process, by which the inventive separators are made, broadly comprises making a first and third microporous membranes, making a second microporous membrane, and bonding together the first, second, and third membranes. Regarding the preferred method for making the membranes, the process requires the following steps: extruding a polymer to form a sheet; annealing the sheet; and stretching the annealed sheet. The specific methods for making these sheets, particularly polyethylene or polypropylene, will be discussed with references to the method of making membranes having a thickness greater than 1 mil. By way of non-limiting example, the following references, each of which is incorporated herein by reference, illustrate the state of the art for making membranes having a thickness greater than 1 mil: U.S. Patent Nos: 3,426,754; 3,558,764; 3,679,538; 3,801,404; 3,801,692; 3,843,761; 3,853,601; 4,138,459; 4,539,256; 4,726,989; and 4,994,335, each of the foregoing is incorporated herein by reference. Knowledge of these methods being assumed, the inventive process for making thin membranes shall be described below by way of explaining the differences between the prior art methods for making standard films (thickness greater than 1 mil) and inventive method for making a thin film (thickness less than about 1/2 mil).

The differences discussed below regarding extrusion, annealing, and stretching are based upon a die configuration of a 27" die equipped with a 70 mil mandrel gap. If the die configuration changes, then the differences will change. For example, if a 6" die is used, the die temperature difference between standard film process and thin film process is much smaller. Regardless of die configuration, thin films require less quench air.

With regard to extrusion conditions, standard film processes typically require stronger quench air conditions and lower extrusion temperatures than thin film processes. For example, the relevant quench conditions for a standard film process include: an air pressure of about 6" H_2O; an air ring gap in the range of 10/64 to 15/64 inches; and an air ring height of 1 to 2 inches; on the other hand, the relevant quench conditions for a thin film process include: an air pressure of about 0.6 to 3.0" H_2O; an air ring gap in the range of 5/64 to 10/64 inches; and a ring height of about 1 to 2 inches. The relevant extrusion conditions for a standard film process (using Exxon's Escorene PP 4292 resin as an example) include: a die temperature in the range of 191 to 198°C and a barrel temperature of 200 to 205°C; on the other hand, the relevant extrusion conditions for a thin film process (using the same material) include: a die temperature in the range of 210°C (for 0.5 mil final product) to 224°C (for 0.33 mil final product) and a barrel temperature of 210°C.

With regard to annealing and stretching conditions, the inter-ply adhesion (measured as peel strength) must be lower than that of the standard process, so that the individual plies do not split (i.e. tear apart) when they are deplied. The ability to resist splitting is proportional to the ply's thickness. Thus, if the plies stick together (due to adhesion) and the stickiness is greater than the split resistance, then the piles cannot be separated (deplied) without splitting. For example, the adhesion of plies having a thickness of about 1 mil should be less than about 15 grams/inch, whereas for 0.5 mil plies, the adhesion should be less than about 8 grams/inch, and for 0.33 mil plies, less than about 5 grams/inch. To lower the adhesion values, the annealing/stretching temperatures for the inventive process are less than those for the standard process. For example, the annealing/stretching temperatures for a polypropylene film would be in the range of 120-125°C (inventive process) compared to the range of 140-150°C (standard process), and for a polyethylene film about 110°C (inventive process) compared to about 115°C (standard process).

To avoid wrinkle formation, trimmed 2-ply films are handled until the trilayer separators are formed. The films' deplying configuration is shown in Figure 2. In Figure 2, a deply and trilayer formation scheme 10 is shown. Scheme 10 includes a ground level layout 12 and an elevated layout 14. Layouts 12 and 14 are identical, but for elevation (to efficiently use space), so only layout 12 will be discussed in detail. Layout 12 comprises three unwind stations 16, 18, and 20. Stations 16 and 20 support rolls of polypropylene microporous membrane (i.e., one roll - 2 plies), and station 18 supports a roll of polyethylene microporous membrane (i.e., one roll - 2 plies). The membranes (i.e., either the PP or PE membranes) in single-ply form are as thin as about 1/3 mil. Membranes or films of this thickness are prone to wrinkling or creasing. To avoid wrinkling or creasing, these membranes are handled (as much as possible), in 2-ply form (about 2/3 mils thick). The polypropylene films 24 and polyethylene films 26 are unwound from their rollers, deplyed, in some cases with the assistance of guide rollers 22, and then replied to form trilayer precursors 28. From scheme 10, four (4) trilayer precursors 28 are formed. At least four trilayer precursors are preferred so to avoid the wrinkle problem and to more efficiently use equipment (economic reasons). A minimum of at least two trilayer precursors is preferred for process economics. The precursors 28 are forwarded to a bonding station

30 (not shown).

Regarding the preferred methods for bonding the membranes together, several bonding methods are contemplated. Broadly, the bonding methods include calendaring, adhering with adhesives, and welding. The application of adhesives may include: air atomizing; gravure/screen printing; hydraulic spraying; and ultrasonic spraying. The choice of adhesive and the rate of adhesive application must be chosen so that the separator's porosity is not adversely effected. The welding technique includes thermal welding and ultrasonic welding. The amount of energy for either welding procedure and the pattern of welds should be chosen so that, among other things, the separator's porosity is not adversely effected. Preferably, bonding is accomplished by calendaring, with nips closed, at a temperature ranging from 125 to 130°C, and a residence time at temperature of about 2 to 10 minutes.

After bonding, the trilayer, shutdown battery separator is rewound for use in the manufacture of batteries, particularly secondary lithium batteries, as is well known in the art.

Further information about the foregoing invention may be obtained from the following non-limiting examples. The test methods referred to herein are set forth below.

Test Methods

Gurley	ASTM-D726(B) Gurley is a resistance to air flow measured by the Gurley densometer (e.g. Model 4120). Gurley is the time in seconds required to pass 10 cc of air through one square inch of product under a pressure of 12.2 inches of water.
Thickness	Method: T411om-83 developed under the auspices of the Technical Association of the Pulp and Paper Industry. Thickness is determined using a precision micrometer with a ½ inch diameter, circular shoe contacting the sample at seven (7) PSI. Ten (10) individual micrometer readings taken across the width of the sample are averaged.
Porosity	ASTM D-2873
Density	ASTM D-792
Puncture Strength	Ten measurements are made across the width of the stretched product and averaged. A Mitech Stevens LFRA Texture Analyzer is used. The needle is 1.65 mm in diameter with 0.5 mm radius. The rate of descent is 2 mm/sec and

	the amount of deflection is 6 mm. The film is held tight in the clamping device with a central hole of 11.3 mm. The displacement (in mm) of the film that was pierced by the needle was recorded against the resistance force (in gram force) developed by the tested film. The maximum resistance force is the puncture strength.
Peel strength	Peel strength is measured using a tension and compression tester to determine the force in grams required to separate two one-inch wide sections of bonded membrane. The peel rate is 6 inches/minute. Three measurements are taken across the web and averaged.
Melt Index	ASTM D 1238; PE: 190°C/2.16 Kg; PP: 230°C/2.16 Kg.

Example

Shutdown trilayer battery separators, as disclosed above, were made in the following manner:

The polypropylene and polyethylene resins used are set forth in TABLES 1 & 2:

TABLE 1

Polypropylene (PP Monopolymer)

	Resin	Density (g/cm^3)	Melt Index (g/10 min)	Supplier
A	Escorene PP4292	0.90	1.4	Exxon Chemical
B	Fina PP 3271	0.905	1.5	Fina Oil & Chemical
C	Fina PP 3281	0.905	1.1	Fina Oil & Chemical
D	Escorene PP4292 (nucleated)	0.90	1.4	Exxon Chemical
E	Escorene PP4372*	0.90	1.4	Exxon Chemical
F	Escorene PP3182	0.90	3.0	Exxon Chemical

*contains an antiblocking agent

TABLE 2

Polyethylene (HDPE)

	Resin	Density (g/cm^3)	Melt Index (g/10 min)	Supplier
G	Fina HDPEGF7750	0.958	0.70	Fina Oil & Chemical
H	Escorene HDZ107	0.964	0.30	Exxon Chemical

The extruder equipment was configured, as set forth in TABLE 3:

TABLE 3

Extruder

	L/D Ratio	Barrel Size	Die Size	Die Opening	Land Length	Blow-up Ratio
E1	24	2.5"	12" or 27"	70 mil	3"	1
E2	24	3.5"	12" or 27"	70 mil	3"	1
E3	30	1.25"	6"	70 mil	3"	1

The resins were extruded as set forth in TABLE 4 to form a tubular precursor films (parison), as set forth in TABLE 4:

TABLE 4

Extrusion Condition

Product	Resin (See Tables 1 & 2)	Extruder/ Die Size (see Table 3)	Extruder Temp (°C)	Melt Temp (°C)	Die Temp (°C)	Air Ring Height (inch)	Quenching Air Press (inches H_2O)	Air Ring Opening (inches)	Thick-ness (mil)	Line Speed (ft/min)
P1	A	E3/6"	200	205	205	1"	1.5"	0.078"	0.38	42
P2	C	E3/6"	205	215	215	1"	1.5"	0.078"	0.38	42
P3	C	E2/27"	230	243	243	1"	1.2"	0.078"	0.38	47
P4	A	E2/27"	210	224	224	1"	1.2"	0.078"	0.38	50
P5	A	E2/12"	220	224	224	1"	1.2"	0.078"	0.38	50
P6	B	E2/27"	210	224	224	1"	1.2"	0.078"	0.38	50
E1	G	E1/27"	200	220	200	1"	1.0"	0.078"	0.38	60
E2	H	E1/12"	180	199	185	1.25"	1.0"	0.094"	0.59	60

The precursor films were annealed in an 8-ply film. This means that since the precursor films are extruded as inflated tubes, when they are collapsed, they created a 2-ply film. Four of these 2-ply films are wound up together to make the 8-ply film. The annealing conditions are set forth below in TABLE 5:

TABLE 5

Annealing Conditions

Product (see Table 4)	Annealing Temp., °C	Annealing Time, Min	Peel Strength (gram/inch)
P1	136	16	-
P2	140	16	-
P3	120	16	-
P4, P5	120	16	2
P6	135	16	0
E1	110	19	1
E2	115	19	1

The annealed precursor films are stretched to form microporous membranes. The annealed precursor films were stretched as 16-ply films (8 rolls of 2 ply films from an extruded tubular precursor). Alternatively, the annealed precursor films maybe stretched as an 8-ply film or 24-ply film. The stretching conditions are set forth in TABLE 6:

TABLE 6

Stretching Conditions

Product (see TABLE 5)	Cold Stretch, Temp (°C)	Cold Stretch*	Hot Stretch Temp (°C)	Hot Stretch*	Hot Relax Temp (°C)	Hot Relax*, [1]	Thick- ness (mil)	Gurley (sec)
P4,P5	ambient	25%	120°C	115%	120°C	40%	0.33	12
P6	ambient	25%	135°C	115%	135°C	40%	0.33	10
E1	ambient	40%	110°C	110%	110°C	50%	0.33	8
E2	ambient	45%	115°C	105%	115°C	40%	0.5	11

* The percentage of the stretching/relaxing was based on the original length before cold stretching

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[1] The relax step indicates that the stretched film is allowed to shrink back.

The microporous membranes, as the 16-ply films, are deplied to 2-ply films. The edge portions of the 2-ply films are trimmed, thereby separating the 2-ply film into individual, detached plies. The PP plies are trimmed 0.5 inches wider than the PE plies.

The trilayer precursor were bonded together by calendaring at 128°C, a line speed of 25 feet/minute, and a residence time at the bonding temperature of about 5-10 minutes.

The trilayer separator, made according to the foregoing example, have the properties set forth in TABLE 7:

TABLE 7

Trilayer Separator Properties

Product	PP/PE/PP (see Table 6)	Thickness (mil)	Gurley (sec)	Puncture Strength (g)	Adhesion (g/cm)
T1	P2/E1/P2	1.02	20	480	4.3
T2	P4,P5/E1/ P4,P5	1.01	29	480	-
T3	P6/E1/P6	1.01	22	483	-
T4	P4,P5/E2/ P4,P5	1.15	30	500	6.5

The properties of a trilayer battery separator are compared to other battery separators (Celgard®-type single-ply PP; Celgard®-type single-ply PE; bilayer PP/PE (see U.S. Patent Application Serial No. 08/348,630 filed December 2, 1994); and cross-ply PE (see U.S. Patent Application Serial No. 08/341,239 filed November 11, 1994) in TABLE 8:

TABLE 8

Comparison of trilayer (PP/PE/PP) with other battery separators

Property	single-ply PP	single-ply PE	bilayer PP/PE	crossply PE/PE	trilayer PP/PE/PP
thickness (mil)	1.0	1.0	1.0	1.0	1.0
Porosity (%)	38	38	38	38	38
Gurley (sec)	25	25	25	25	25
Shutdown temp (°C)	165	132	132	132	132
Shutdown temp range (°C)	-	20	35	20	35
puncture strength (g)	380	290	490 (PP) 300 (PE)	490	480

The present invention maybe embodied in other specific forms without departing from the spirit or essential attributes thereof, and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification as indicating the scope of the invention.

I claim:

1. A shutdown, trilayer battery separator comprising a first and a third microporous polypropylene membranes sandwiching a microporous polyethylene membrane.

2. The battery separator of claim 1 further comprising a thickness ranging from about 0.5 to about 1.5 mils.

3. The battery separator of claim 2 further comprising a thickness of about 1 mil.

4. The battery separator of claim 1 wherein said puncture strength is greater than or equal to about 450 grams.

5. The battery separator of claim 4 wherein said puncture strength is greater than or equal to about 480 grams.

6. The battery separator of claims 1 further comprising a peel strength of greater than or equal to 4 grams per inch.

7. The battery separator of claim 6 wherein said peel strength is greater than or equal to 6 grams per inch.

8. A battery comprising the separator of claim 1.

9. A shutdown battery separator comprising a first and a third microporous polypropylene membranes sandwiching a microporous polyethylene membrane, said separator having: a thickness in the range of about 0.5 mils to about 1.5 mils; a puncture strength greater than or equal to about 450 grams; and a peel strength of greater than 4 grams per inch.

10. The shutdown separator according to claim 9 wherein said thickness is about 1 mil.

11. The shutdown separator according to claim 9 wherein said puncture strength is greater than or equal to about 480 grams.

12. The shutdown separator according to claim 9 wherein said peel strength is greater than or equal to about 6 grams per inch.

13. A battery comprising the separator of claim 9.

14. A method for making a microporous membrane having a thickness less than about 0.5 mils comprises the steps of:

extruding a parison;

collapsing the parison onto itself to form a flat sheet comprising two plies;

annealing the flat sheet;

stretching the flat sheet; and

winding up the flat sheet , an adhesion force between the two plies being less than 8 grams per inch.

15. The method according to claim 14 for making a microporous membrane having a thickness less than or equal to about 0.33 mils wherein the adhesion force is less than 5 grams per inch.

16. The method according to claim 14 further comprising the step of quenching the extruded parison with a gas having an air pressure ranging from 0.6 to 3.0 inches of water.

17. A method of making a trilayer shutdown battery separator comprising the steps of:

providing a first and third flat sheet comprising two plies of microporous polypropylene membranes made according to the method of claim 14;

providing a second flat sheet comprising two plies of a microporous polyethylene membrane made according to the method of claim 14;

deplying the first and the third flat sheets of microporous polypropylene membranes;

deplying the second flat sheet of polyethylene microporous membranes

replying the individual plies to form a polypropylene - polyethylene - polypropylene structure;

bonding the structure to form a trilayer separator; and

winding - up the separator.

18. The method according to claim 17 wherein bonding comprises calendaring or adhering with adhesives or welding.

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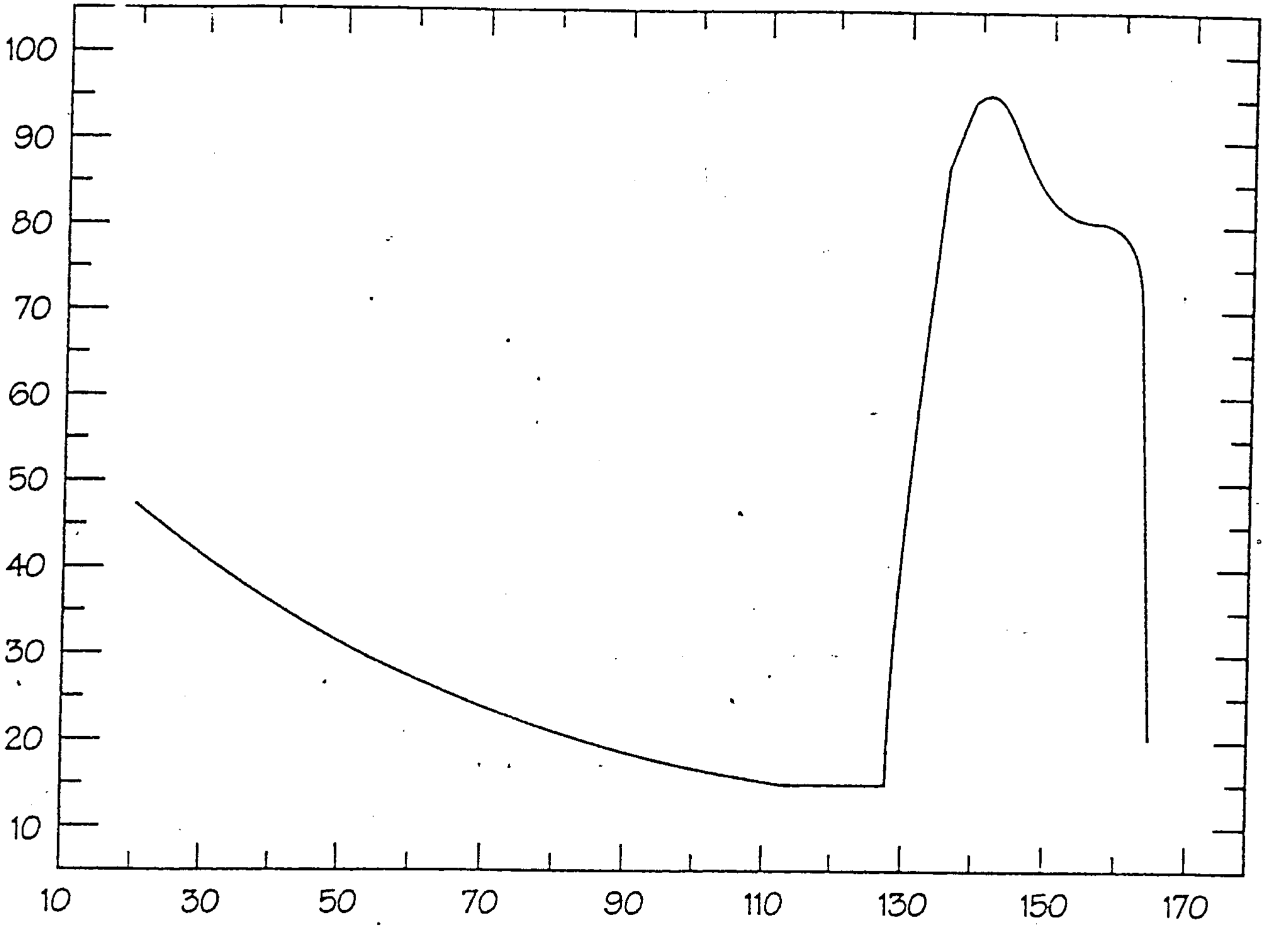

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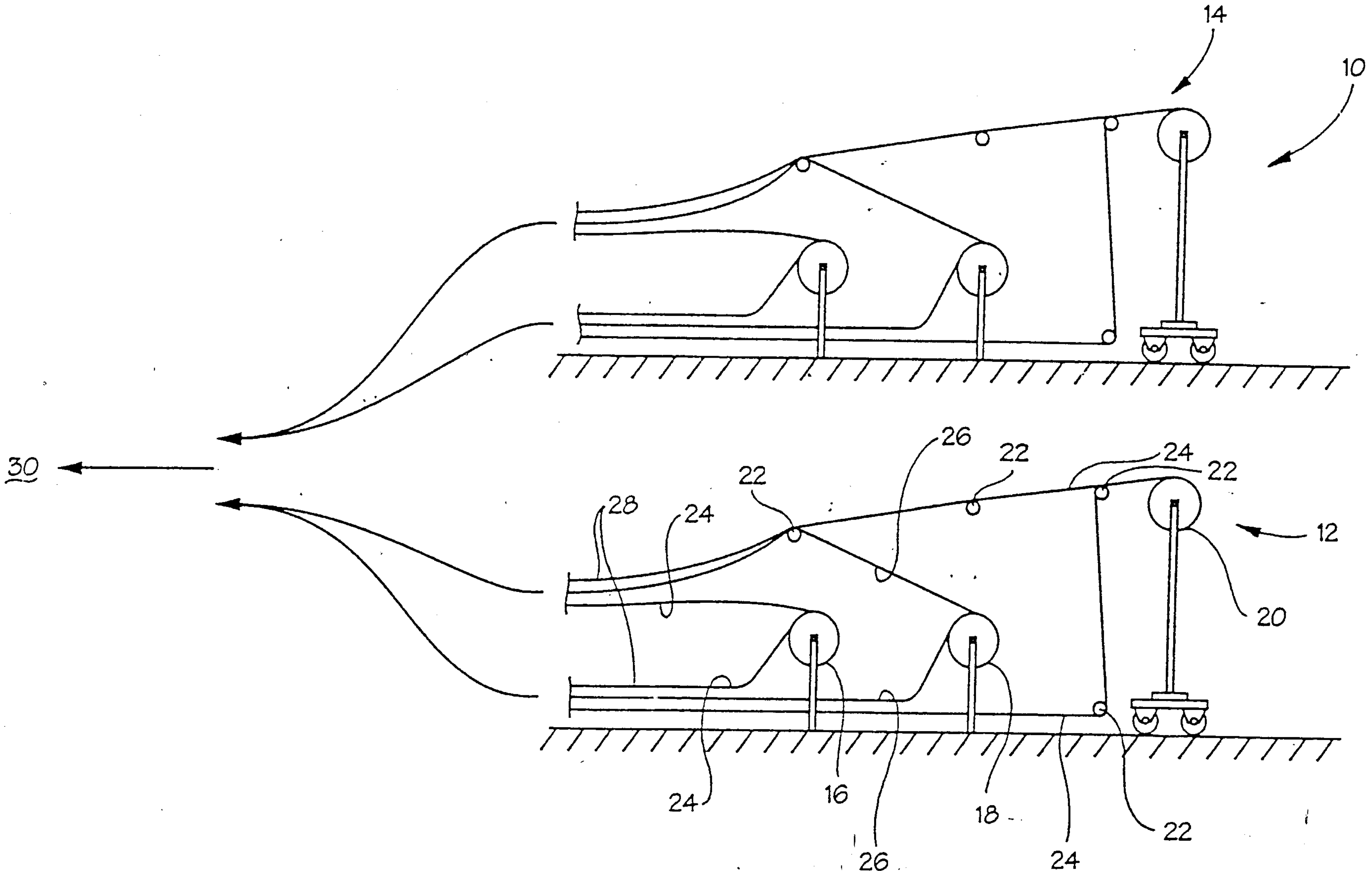

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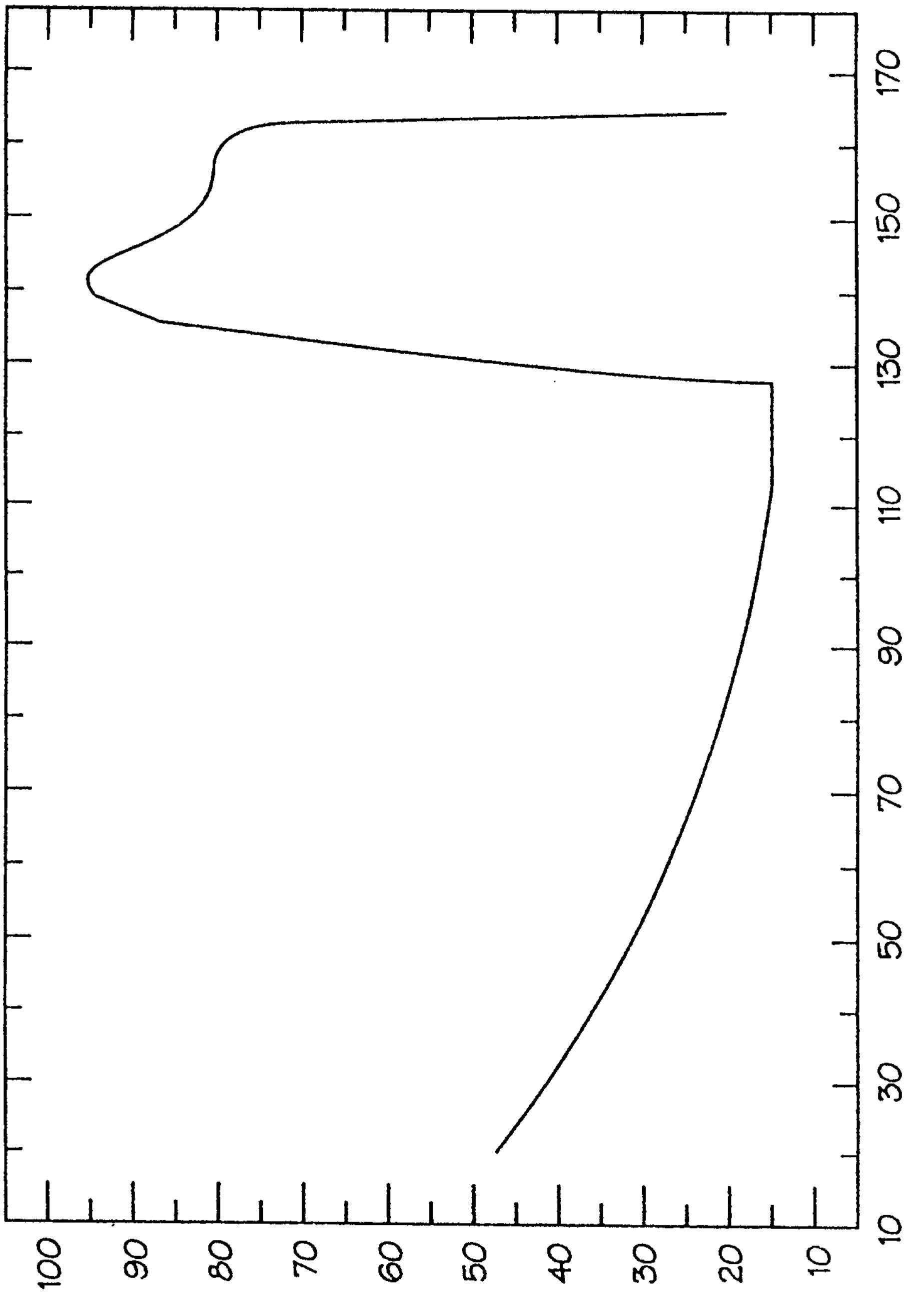

Fig. 1

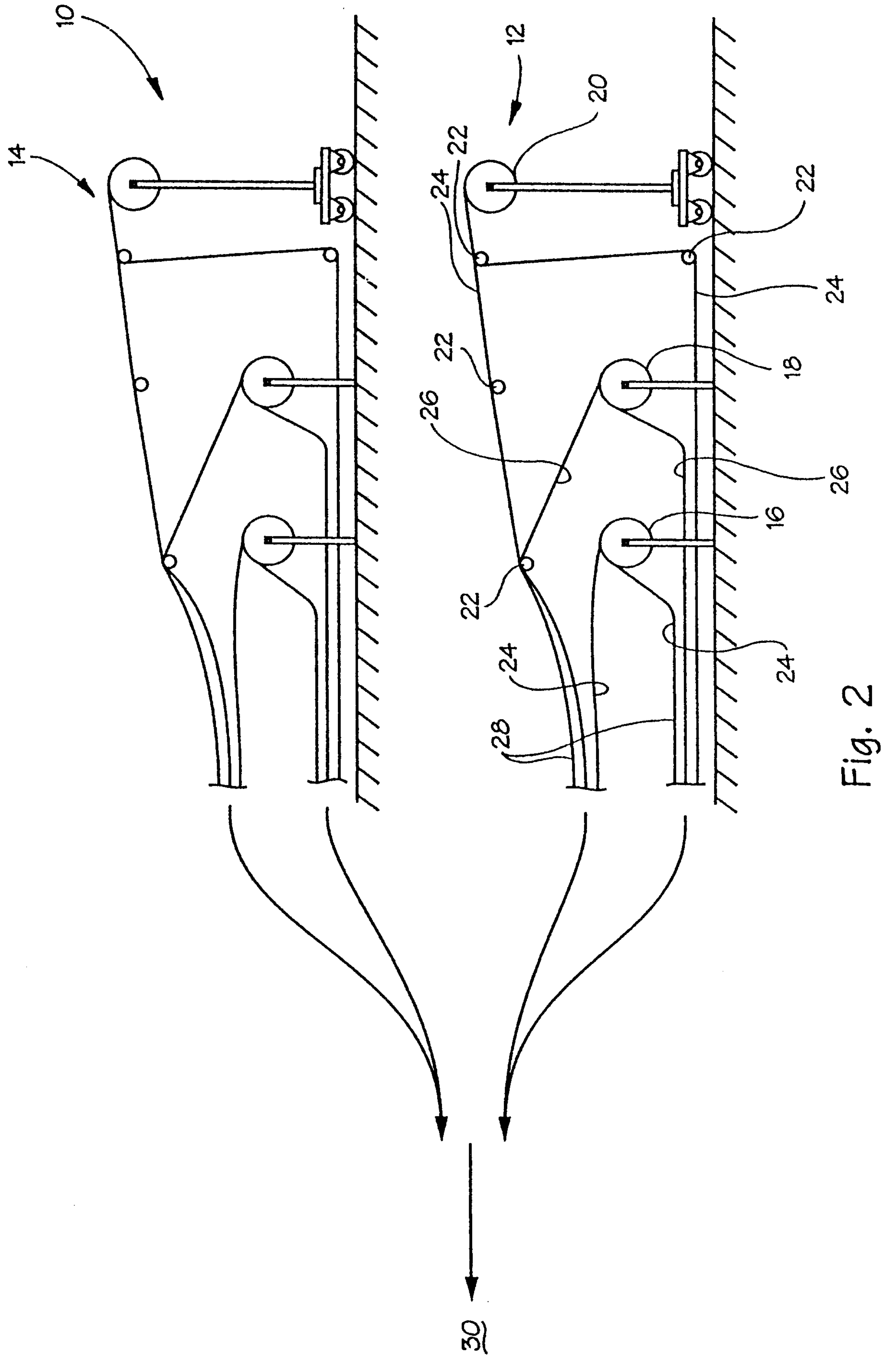

Fig. 2