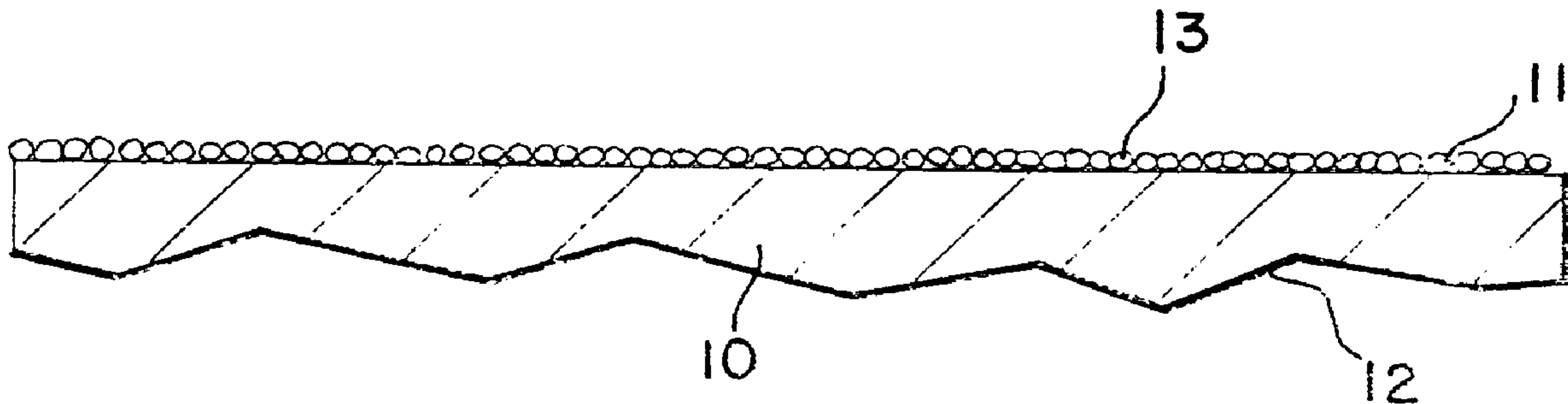




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(54) Titre : PAPIER METALLIQUE ET LAMINE POUR CARTES DE CIRCUIT IMPRIME ET LEURS METHODES DE FABRICATION  
 (54) Title: DRUM-SIDE TREATED METAL FOIL AND LAMINATE FOR USE IN PRINTED CIRCUIT BOARDS AND METHODS OF MANUFACTURE



(57) **Abrégé/Abstract:**

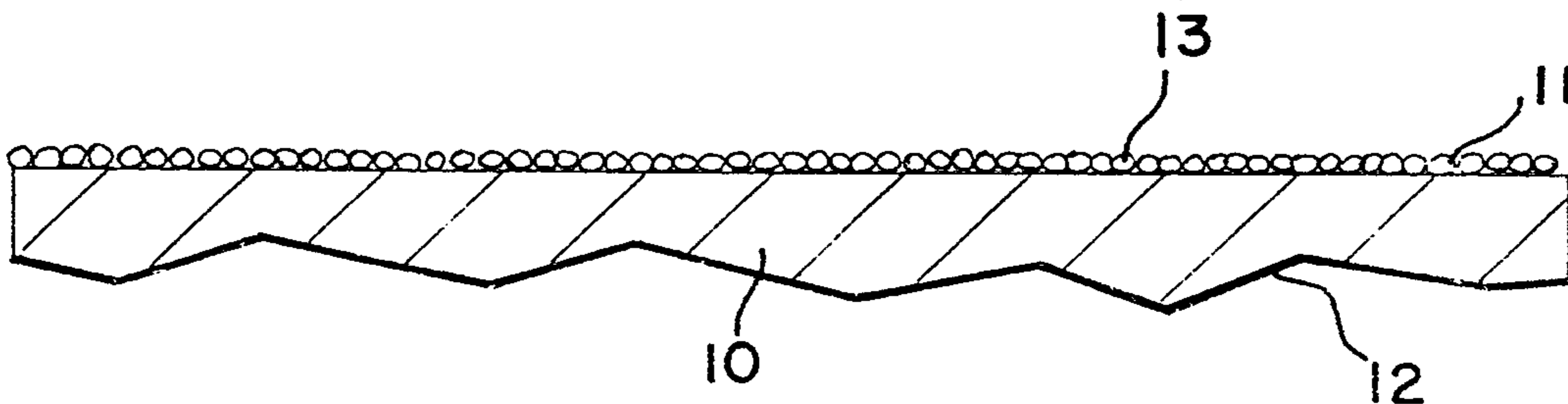
Drum or smooth side-treated metal foil can be used either as an intermediate product for use in the manufacture of laminate or as a part of the finished laminate to be used in the manufacture of multi-layer printed circuit board (PCB) packages. By treating the drum or smooth side (11) of metal foil (10) with a bond strength enhancer (13) rather than treating the matte side or rough side (12), or both sides, several time-consuming and costly steps can be bypassed in the manufacture of multi-layer printed circuit boards (PCB) while the integrity of the metal foil, laminate and multi-layer PCB are not compromised and are actually enhanced by way of improved impedance control and adhesion characteristics after relamination. This novel foil can be initially bonded to substrate on either side before circuit formation and can be used either as an internal foil layer or as a foil cap. The invention includes methods of manufacture of the metal foil, laminate and multi-layer printed circuit board. A variation of the invention involves a component or tool for use in manufacturing articles such as printed circuit boards. The component is a temporary laminate constructed of one or more sheets of drum-side-treated copper foil mounted on a sheet of aluminium. The copper foil, which, in a finished printed circuit board, will constitute a functional element, has a drum-side, which has been subjected to an adhesion-promoting treatment, and a rough side, which has not been subjected to the adhesion-promoting treatment. The sheet of aluminium constitutes a discardable or reusable element. Either surface (treated drum-side or untreated matte side) of each copper sheet can be bonded to the aluminium, depending on which embodiment of the basic invention is being used. The side of the copper foil not bonded to the aluminium will be bonded to the resin in the next step.



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<b>(21) International Application Number:</b> PCT/US94/02309 <b>(22) International Filing Date:</b> 2 March 1994 (02.03.94) <b>(30) Priority Data:</b> 08/027,620 5 March 1993 (05.03.93) US 08/176,750 3 January 1994 (03.01.94) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 08/176,750 (CON) Filed on 3 January 1994 (03.01.94) <b>(71) Applicant (for all designated States except US):</b> POLYCLAD LAMINATES, INC. [US/US]; 40 Industrial Park Drive, West Franklin, NH 03235 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> SEIP, D., Eric [US/US]; 27548 Jasmine Avenue, Mission Viejo, CA 92692 (US). <b>(74) Agents:</b> BLODGETT, Gerry, A. et al.; 43 Highland Street, Worcester, MA 01609 (US).	<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). <p style="text-align: center; font-size: 2em;"><b>2157587</b></p> <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <b>(88) Date of publication of the international search report:</b> 27 October 1994 (27.10.94)	

**(54) Title:** DRUM-SIDE TREATED METAL FOIL AND LAMINATE FOR USE IN PRINTED CIRCUIT BOARDS AND METHODS OF MANUFACTURE

**(57) Abstract**

Drum or smooth side-treated metal foil can be used either as an intermediate product for use in the manufacture of laminate or as a part of the finished laminate to be used in the manufacture of multi-layer printed circuit board (PCB) packages. By treating the drum or smooth side (11) of metal foil (10) with a bond strength enhancer (13) rather than treating the matte side or rough side (12), or both sides, several time-consuming and costly steps can be bypassed in the manufacture of multi-layer printed circuit boards (PCB) while the integrity of the metal foil, laminate and multi-layer PCB are not compromised and are actually enhanced by way of improved impedance control and adhesion characteristics after relamination. This novel foil can be initially bonded to substrate on either side before circuit formation and can be used either as an internal foil layer or as a foil cap. The invention includes methods of manufacture of the metal foil, laminate and multi-layer printed circuit board. A variation of the invention involves a component or tool for use in manufacturing articles such as printed circuit boards. The component is a temporary laminate constructed of one or more sheets of drum-side-treated copper foil mounted on a sheet of aluminium. The copper foil, which, in a finished printed circuit board, will constitute a functional element, has a drum-side, which has been subjected to an adhesion-promoting treatment, and a rough side, which has not been subjected to the adhesion-promoting treatment. The sheet of aluminium constitutes a discardable or reusable element. Either surface (treated drum-side or untreated matte side) of each copper sheet can be bonded to the aluminium, depending on which embodiment of the basic invention is being used. The side of the copper foil not bonded to the aluminium will be bonded to the resin in the next step.

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**DRUM-SIDE TREATED METAL FOIL AND LAMINATE FOR USE IN  
PRINTED CIRCUIT BOARDS AND METHODS OF MANUFACTURE****FIELD OF INVENTION**

Drum or smooth side-treated metal foil can be used either as an  
5 intermediate product for use in the manufacture of laminate or as a part of the  
finished laminate to be used in the manufacture of multi-layer printed circuit board  
(PCB) packages. By treating the drum or smooth side of metal foil with a bond  
strength enhancer rather than treating the matte side or rough side, or both sides,  
several time-consuming and costly steps can be bypassed in the manufacture of  
10 multi-layer printed circuit boards (PCB) while the integrity of the metal foil,  
laminate and multi-layer PCB are not compromised and are actually enhanced by  
way of improved impedance control and adhesion characteristics after  
relamination. This novel foil can be initially bonded to substrate on either side  
before circuit formation and can be used either as an internal foil layer or as a foil  
15 cap. The invention includes methods of manufacture of the metal foil, laminate  
and multi-layer printed circuit board.

**BACKGROUND OF THE INVENTION**

Metal foil, primarily copper foil, has long been manufactured for use in  
printed circuit boards. Of the various types of metal foil used, electrodeposited  
20 foil is the most common. Electrodeposited copper foil is electroplated from a  
copper plating solution onto a revolving drum, typically, with a titanium or  
stainless steel surface acting as the cathode in the plating process. The matte side,  
or side away from the drum surface of electrodeposited foil is rough which  
enhances the adhesive strength, especially when coupled with subsequent adhesion  
25 enhancing treatments. The drum side of the electroplated foil is very smooth, and  
has a shiny appearance, and is regarded as a poor adhesion surface.

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Typical adhesion promoting treatments consist of plating additional copper and zinc onto the matte side of the foil. Other agents such as silanes are also being used. The foil is then processed through a stain proofing solution to act as an oxidation retardant of the metal surface.

5 An alternate foil product which has also been manufactured historically is what is known in the circuit board industry as "double-treat" metal foil. This foil is electroplated identically to what is described in the preceding paragraphs but it is typically run through the adhesion promoting treating line a second time and plated with additional adhesion promoters on the drum or shiny side of the foil.

10 The purpose of this product is to replace a subsequent step known as the oxidizing process in the manufacture of printed circuit boards. Problems with this double-treat product are extremely common at each of the discrete steps in the circuit board process, namely, at the metal foil manufacturer step, the laminate manufacturer step and the multi-layer printed circuit board (PCB) manufacturer

15 step. The double-treat metal foil typically has a much higher scrap rate than single side treated foils and additional processing steps are required, thus increasing both cycle times and costs. At the laminate and PCB manufacturer, handling problems can drive scrap rates to unacceptably high levels. The problem is so significant that only a very limited number of manufacturers will even

20 attempt to use this double-treat product.

The foil-and-substrate laminate for use in the printed circuit board industry can be constructed from a variety of substrates including paper, glass, and TEFLON. These substrates are coated or impregnated in a continuous fashion with a resin system to facilitate adhesion with the metal foil which will

25 subsequently be clad to the substrate on one or both sides in a process referred to in the PCB industry as pressing. This unclad substrate shall be referred to as prepreg.

Both the prepreg and the metal foil are typically sheeted although technology does exist for "continuous lamination". The laminate can be

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manufactured with either single or multiple plies of prepreg which will result in various thicknesses as dictated by customer and/or design criteria. The prepreg and metal foil are bonded together by means of heat and pressure under controlled conditions which depend on the required product properties.

5           The pressed units, referred to in the industry as laminates, must then have the edges trimmed off. Oftentimes, smaller units are fabricated from the pressed unit. These steps require additional handling and any minor surface damage may result in the rejection of laminate clad with "double treat" metal foil. This minor surface damage is typically aesthetic only and will not negatively affect the  
10 functionality of the finished printed circuit board. Minor surface damage on single side treated metal foil can be masked by a subsequent processing step referred to as oxidizing, thus resulting in higher processing yields.

          The next typical step of multi-layer PCB manufacture is to remove the oxidation retardant, which was applied by the metal foil manufacturer. This  
15 removal is accomplished by means of a mild acid cleaner, a mechanical scrubbing of the surface or a combination of both. In the industry, this step is referred to as the scrubbing or cleaning process.

          Next, the cleaned panel is laminated with a polymeric light sensitive photo resist. An image is printed onto the photo resist by means of exposure to intense  
20 light under controlled conditions. The unexposed film is then chemically removed from the metal surface and the now exposed metal surface is chemically etched off. The remaining photo resist is stripped off through additional chemical processing. The result is a pattern of conductive lands separated by insulative grooves to form a printed circuit.

25           These etched laminates, hereafter referred to as inner layers, are inspected for defects in the metal circuitry and the substrate. This inspection typically is done by automated optical inspection equipment commonly referred to as AOI. The technologies for various brands of AOI equipment differ. Some equipment

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inspects the substrate surface to detect flaws. others use a reflective technology where the metal foil surface is inspected for flaws. One problem experienced by all users of reflective technology is that when any oxidation occurs on the metal surface, it is detected as a flaw. After the automated inspection, human operators  
5 verify all defects. Almost more times than not, a flaw detected by the AOI equipment is not a functional flaw and the human verifier will accept the inner layer.

After inspection, the inner layers will undergo an additional chemical process known in the industry as the oxidizing process. Under current industry  
10 practices, the typical inner layer has the drum or smooth side of the metal exposed to the environment and the matte or rough side imbedded within the prepreg. This smooth outer surface alone does not offer sufficient surface topography to allow for subsequent relamination with acceptable adhesion characteristics. The purpose of the oxidizing process is to "grow", under controlled conditions, an  
15 oxide crystal layer which is designed to increase the surface area and thus create acceptable adhesion characteristics, on the smooth surface, for the subsequent relamination process.

An optional, but widely used and expensive final step of the oxide process, is a post dip bath which essentially reduces the valence of the copper to a +1  
20 from a +2 state. The benefit achieved from this is the elimination of what is known as "pink ring", a term widely used in the industry. Pink ring is the dissolution of the copper oxide around drilled holes, forming a pink ring of exposed, bare copper. It is cause for rejection of the part.

A typical oxide process consists of many different chemical baths including  
25 but not limited to one or more cleaning baths, a microetch bath to aid in increasing surface topography, an oxide bath where the oxide crystals are actually formed and numerous pre-dip and rinse baths, followed by a post-dip, reduction bath. This process is difficult to optimize, expensive to operate and extremely time consuming. As noted previously, laminate which is clad with "double treat"

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metal foil does not require this processing step.

After this operation, oxidized inner layers (or inner layers clad with double treated metal foil) are ready to be combined with additional prepreg material laminated on both sides (and additional inner layers if required) and generally, 5 clad on the outermost surfaces with additional metal foil. This package will be heated and pressed in a similar fashion to that of the laminate manufacture described above. Among the critical characteristics of this semifinished multi-layer printed circuit board is the ability of the many different components used in its manufacture to remain firmly bonded together. The adhesion strength of both 10 the metal foil treatment and the oxide play integral roles in the reliable life of a multi-layer printed circuit board. Typically, the weakest link in this package is the oxide adhesion to the relamination prepreg. This weak point many times results in product failure in the field. These and other difficulties experienced with the prior art devices have been obviated in a novel manner by the present 15 invention.

It is an object of the present invention to provide a product which can reduce multi-layer printed circuit board manufacture cycle time through the elimination of several manufacturing steps. A direct consequence of this objective is the reduction in costs associated with the manufacture of multi-layer printed 20 circuit boards.

A second, equally important objective of the present invention is to improve the reliability of the overall multi-layer circuit board package. By strengthening the weakest adhesion link which exists in today's technology, the oxide, the finished product will be less prone to delamination when operating in 25 harsh conditions or normal conditions for long periods of time.

One additional consideration was taken into account as an objective of the invention. This is the systematic reduction of chemical processes required in the manufacture of multi-layer printed circuit boards. This objective will reduce the

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amount of hazardous waste generated by all circuit board shops which will utilize this means of manufacture. Additional direct costs will be reduced and regulatory fees should also decline. Our environment will also benefit as a result.

5 With these and other objects in view, as will be apparent to those skilled in the art, the invention resides in the combination of parts set forth in the specification and covered by the claims appended hereto.

### SUMMARY OF THE INVENTION

10 Drum or smooth side-treated metal foil can be used either as an intermediate product for use in the manufacture of laminate or as a part of the finished laminate to be used in the manufacture of multi-layer printed circuit board (PCB) packages. By treating the drum or smooth side of metal foil with a bond strength enhancer rather than treating the matte side or rough side, or both sides, several time-consuming and costly steps can be bypassed in the manufacture of multi-layer printed circuit boards (PCB) while the integrity of the metal foil, 15 laminate and multiple layer PCB are not compromised and are actually enhanced by way of improved impedance control and adhesion characteristics after relamination. This novel foil can be initially bonded to substrate on either side before circuit formation and can be used either as an internal foil layer or as a foil cap. The invention includes methods of manufacture of the metal foil, laminate 20 and multiple layer printed circuit board.

A variation of the invention involves a component or tool for use in manufacturing articles such as printed circuit boards. The component is a temporary laminate constructed of one or more sheets of drum-side-treated copper foil mounted on a sheet of aluminum. The copper foil, which, in a finished 25 printed circuit board, will constitute a functional element, has a drum-side, which has been subjected to an adhesion-promoting treatment, and a rough side, which has not been subject to the adhesion-promoting treatment. The sheet of aluminum constitutes a discardable or reusable element. Either surface (treated drum-side

or untreated matte side) of each copper sheet can be bonded to the aluminum depending on which embodiment of the basic invention is being used. The side of the copper foil not bonded to the aluminum will be bonded to the resin in the next step.

5

In one embodiment, the invention provides a method of forming a printed circuit board consisting of: depositing a quantity of an electrically conductive material onto a smooth forming surface to form a foil having a first smooth surface which forms against the forming surface, and a second matte surface which forms  
10 away from the forming surface, plating an adhesion promoting layer on said first surface, treating the plated foil with an oxidation retardant, bonding one of said plated first surface and said unplated second surface of said treated foil which carries said oxidation retardant to a first electrically insulative substrate, and forming a circuit pattern on the other of said first surface and said second surface of  
15 said treated foil which carries said oxidation retardant by the application and selective removal of a photo-resist material.

In a further embodiment, the invention provides a method which includes providing a tool sheet which constitutes a discardable element, bonding one of the  
20 plated first surface and the unplated second surface to the tool sheet to form a temporary laminate, bonding the other of the plated first surface and the unplated second surface to the first electrically insulative substrate, and terminating the bond between the tool sheet and the foil and separating the tool sheet from the foil.

25 In a further embodiment, the nominal dielectric thickness range of the first electrically insulative substrate is between 0.00019 of an inch and 0.02510 of an inch.

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It should be understood that, although the foil will sometimes be designated as copper herein, because copper is the most common material from which to form the foil, any electrically conductive sheet material, including copper alloys, are encompassed by the disclosure.

5

### BRIEF DESCRIPTION OF THE DRAWINGS

The character of the invention, however, may be best understood by reference to one of its structural forms, as illustrated by the accompanying drawings, in which:

10

FIG. 1 is a diagrammatic sectional view of a foil treated in the "single-treat" method of the prior art,

FIG. 2 is a diagrammatic sectional view of a foil treated in the "double-treat" method of the prior art,

15

FIG. 3 is a diagrammatic sectional view of a foil embodying the principles of the present invention,

FIG. 4 is a diagrammatic sectional view of a step in a first embodiment of the process of the present invention in which the foil is formed on a smooth surface,

20

FIG. 5 is a diagrammatic sectional view of step in a first embodiment of the process of the present invention in which the smooth side of the foil is treated with an adhesion enhancing plating,

FIG. 6 is a diagrammatic sectional view of a step in a first embodiment of the process of the present invention in which the treated smooth surface of the foil is bonded to a substrate,

25

FIG. 7 is a diagrammatic sectional view of a step in a first embodiment of the process of the present invention in which the matte surface of the foil is coated

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with photo resist without the need for a prior scrubbing process.

FIG. 8 is a diagrammatic sectional view of a step in a first embodiment of the process of the present invention in which the matte surface, from which the photo resist has been removed, is treated with an oxidizing process without the  
5 need for a prior microetch and rinse process,

FIG. 9 is a diagrammatic sectional view of a step in a first embodiment of the process of the present invention in which a second substrate is bonded to the oxidized matte side of the foil.

FIG. 10 is a diagrammatic sectional view of a step in a second embodiment  
10 of the process of the present invention in which the foil is formed on a smooth surface,

FIG. 11 is a diagrammatic sectional view of a step in a second embodiment of the process of the present invention in which the smooth side of the foil is treated with an adhesion enhancing plating,

15 FIG. 12 is a diagrammatic sectional view of a step in a second embodiment of the process of the present invention in which the treated smooth surface of the foil is bonded to a substrate,

FIG. 13 is a diagrammatic sectional view of a step in a second embodiment of the process of the present invention in which the matte surface of the foil is  
20 coated with photo resist without the need for a prior scrubbing process,

FIG. 14 is a diagrammatic sectional view of a step in a second embodiment of the process of the present invention in which the photo resist has been removed from the matte surface. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, it would now be complete, without the next step.

25 FIG. 15 is a diagrammatic sectional view of a step in a second embodiment of the process of the present invention in which a second substrate is bonded to the unoxidized matte side of the foil.

FIG. 16 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which the foil is formed on a smooth  
30 surface,

FIG. 17 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which the smooth side of the foil is

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treated with an adhesion enhancing plating,

FIG. 18 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which the untreated matte surface of the foil is bonded to a substrate,

5 FIG. 19 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which the treated smooth surface of the foil is coated with photo resist without the need for a prior scrubbing process,

10 FIG. 20 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which the photo resist has been removed from the matte surface. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, it would now be complete, without the next step,

FIG. 21 is a diagrammatic sectional view of a step in a third embodiment of the process of the present invention in which a second substrate is bonded to the treated smooth side of the foil,

15 FIG. 22 is a flow chart showing a process embodying a second major aspect of this invention,

FIGS. 23-44 are diagrammatic sectional views of various foil-tool combinations and the steps in various processes involved in this variation of this invention,

20 FIG. 23 shows cross-sectional view of a single-sided tool 50 of the present invention, with the untreated matte side of the foil 52 toward the plate 51,

FIG. 24 shows a variation of the tool shown in FIG. 23, the variation being that the tool 60 in FIG. 24 has the treated drum-side of the foil toward the plate 61,

25 FIG. 25 shows cross-sectional view of a double-sided tool 70 of the present invention, with the untreated matte side of the foil 72' and 72" toward the plate 71,

30 FIG. 26 shows a variation of the tool shown in FIG. 25, the variation being that the tool 80 in FIG. 26 has the treated drum-sides of the foils toward the plate 81,

FIGS. 27-32 show a fourth embodiment of the process of the present invention,

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FIG. 27 shows a step in which the foil 110 is formed on a smooth surface 114,

FIG. 28 shows a step in which the smooth side 111 of the foil 110 is treated with an adhesion enhancing plating 113, and the matte side 112 of the foil 5 110 is mounted on the tool 101,

FIG. 29 shows a step in which the treated smooth surface 111 of the foil 110 is bonded to a first surface 115 of a substrate 116, and then the tool 101 is removed from the foil 110,

FIG. 30 shows a step in which the matte surface 112 of the foil 110 is 10 coated with photo resist 117 without the need for a prior scrubbing process,

FIG. 31 shows a step in which the matte surface 112, from which the photo resist has been removed, is treated with an oxidizing process, to form an oxide layer 118, without the need for a prior microetch and rinse process,

FIG. 32 shows a step in which a second substrate 119 is bonded to the 15 oxidized matte side 112 of the foil 110,

FIGS. 33-38 show a fifth embodiment of the process of the present invention,

FIG. 33 shows a step in which the foil 120 is formed on a smooth surface 124,

FIG. 34 shows a step in which the smooth side 121 of the foil 120 is 20 treated with an adhesion enhancing plating 123, and the matte side 122 of the foil 120 is mounted on tool sheet 102 or plate, preferably of aluminum,

FIG. 35 shows a step in which the treated smooth surface 121 of the foil 120 is bonded to a first surface 125 of a substrate 126 after which the tool 102 can 25 be removed,

FIG. 36 shows a step in which the matte surface 122 of the foil 120 is coated with photo resist 127 without the need for a prior scrubbing process,

FIG. 37 shows a step in which the photo resist 127 has been removed from the matte surface 122,

FIG. 38 shows a step in which a second substrate 129 is bonded to the 30 untreated and unoxidized matte side 122 of the foil 120,

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FIGS. 39-44 show a sixth embodiment of the process of the present invention,

FIG. 39 shows a step in which the foil 130 is formed on a smooth surface 134,

5 FIG. 40 shows a step in which the smooth side 131 of the foil 130 is treated with an adhesion enhancing plating 133, and then the treated smooth side 131 of the foil 130 is bonded to a tool 103,

FIG. 41 shows a step in which the untreated matte surface 132 of the foil 130 is bonded to a first surface 135 of a substrate 136, after which, the tool 103  
10 is removed,

FIG. 42 shows a step in which the treated smooth surface 131 of the foil 130 and plated layer 133 are coated with photo resist 137 without the need for a prior scrubbing process,

FIG. 43 shows a step in which the photo resist 137 has been removed from  
15 the treated smooth surface 131, and

FIG. 44 shows a step in which a second substrate 139 is bonded to the treated smooth side 131 of the foil 130.

### **DESCRIPTION OF THE PREFERRED EMBODIMENT**

The details of the invention, however, may be best understood by reference  
20 to its three structural forms, as illustrated by the accompanying drawings. The first embodiment is characterized by an oxidized matte surface facing out, and is shown in FIGS. 4-9. The second embodiment is characterized by an unoxidized matte surface facing out, and is shown in FIGS. 10-15. The third embodiment is characterized by a treated smooth surface facing out, and is shown in FIGS. 16-  
25 21. Each embodiment has two subembodiments; one in which the foil ends up sandwiched within a multi-layer PCB, and a second in which the foil ends up as a cap or outer foil layer on the outer surface of the PCB. The cap subembodiment would apply to both single- and double-sided (clad) PCB's, which are not considered "multi-layer" PCB's.

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FIGS. 1-21 are diagrammatic sectional views of various foils and the steps in various processes. FIG. 1 shows a foil treated in the "single-treat" method of the prior art. The foil 1 has a smooth side 2 and a matte side 3. The matte side 3 is treated by plating with copper-zinc particles 4. FIG. 2 shows a foil treated in the "double-treat" method of the prior art. The foil 5 has a smooth side 6 and a matte side 7. Both the smooth side 6 and the matte side 7 are treated by plating with copper-zinc particles 8. FIG. 3 shows a foil embodying the principles of the present invention. The foil 10 has a smooth side 11 and a matte side 12. The smooth side 11 is treated by plating with copper-zinc particles 13.

10 FIG. 4 shows a step in a first embodiment of the process of the present invention in which the foil 10 is formed on a smooth surface 14. FIG. 5 shows a step in which the smooth side 11 of the foil is treated with an adhesion enhancing plating 13. FIG. 6 shows a step in which the treated smooth surface 11 of the foil 10 is bonded to a first surface 15 of a substrate 16. FIG. 7 shows  
15 a step in which the matte surface 12 of the foil 10 is coated with photo resist 17 without the need for a prior scrubbing process. FIG. 8 shows a step in which the matte surface 12, from which the photo resist has been removed, is treated with an oxidizing process, to form an oxide layer 18, without the need for a prior microetch and rinse process. It will be understood by those skilled in the art that  
20 if this foil is a cap or outside foil layer, it would not need the oxidizing treatment and would be complete without it and without the next step. FIG. 9 shows a step in which a second substrate 19 is bonded to the oxidized matte side 12 of the foil 10.

FIG. 10 shows a step in a second embodiment of the process of the present invention in which the foil 20 is formed on a smooth surface 24. FIG. 11 shows a step in which the smooth side 21 of the foil 20 is treated with an adhesion enhancing plating 23. FIG. 12 shows a step in which the treated smooth surface 21 of the foil 20 is bonded to a first surface 25 of a substrate 26. FIG. 13 shows a step in which the matte surface 22 of the foil 20 is coated with photo resist 27  
30 without the need for a prior scrubbing process. FIG. 14 shows a step in which

(13)

the photo resist 27 has been removed from the matte surface 22. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, you would not have a subsequent relamination over this layer, so the next step would not be necessary. FIG. 15 shows a step in which a second substrate 29 is  
5 bonded to the untreated and unoxidized matte side 22 of the foil 20.

FIG. 16 shows a step in a third embodiment of the process of the present invention in which the foil 30 is formed on a smooth surface 34. FIG. 17 shows a step in which the smooth side 31 of the foil 30 is treated with an adhesion  
10 enhancing plating 33. FIG. 18 shows a step in which the untreated matte surface 32 of the foil 30 is bonded to a first surface 35 of a substrate 36. FIG. 19 shows a step in which the treated smooth surface 31 of the foil 30 is coated with photo resist 37 without the need for a prior scrubbing process. FIG. 20 shows a step in which the photo resist 37 has been removed from the treated smooth surface 31.  
15 It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, you would not have a subsequent relamination over this layer, so the next step would not be necessary. FIG. 21 shows a step in which a second substrate 39 is bonded to the treated smooth side 31 of the foil 30.

In inventing a system which achieves the objectives of the present  
20 invention, processability was constantly emphasized. The manufacture of the untreated metal foil is identical to current technology. The adhesion promoting treatment chemistry and oxidation retardant treatments are also the same. The primary difference is the application of said adhesion promoting treatment. Current technology requires that the matte side of the metal foil be treated with  
25 the bond enhancers or, on "double treat" metal foil, both the matte and drum sides are treated with the bond enhancers. The present invention provides that only the drum side of the metal foil be treated with the bond enhancers. This is exactly opposite of current industry practices for single treat metal foils.

It is important to note that this change in the side of the foil that is treated  
30 requires no additional processing equipment or steps by the metal foil

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manufacturer to produce this product as opposed to existing matte side treated foil. This invention performs best with a "low profile" foil, a foil with the matte side  $Rz < 10.2$  microns as recognized by current industry standards. Very low profile foil ( $Rz < 5.1$  microns) and standard foil (no  $Rz$  requirement) also perform  
5 acceptably.  $Rz$  is the mean peak-to-valley height of the matte teeth.

The invention employs a single-side-treated metal foil where the adhesion enhancing treatment is applied only to the drum or smooth side of the foil. This is exactly opposite of current industry practices. See Figure 3 for the invention and Figure 1 and 2 for prior technology. Current industry practices of  
10 antioxidation treatment application would remain essentially identical.

This metal foil is used by a laminate manufacturer to produce a metal clad laminate for use, after circuit pattern formation, in the multi-layer printed circuit board industry. The laminate manufacturer will also continue to follow virtually identical processing steps as in the manufacture of single treat metal foil clad  
15 laminate. The laminator will press the treated drum surface of the foil against the prepreg in the lamination process. This is the only significant processing difference used in the lamination step of the process.

The printed circuit board manufacturer will experience several significant changes in existing processes. The first step which can be eliminated in the multi-  
20 layer process was described previously as the scrubbing or cleaning process, which normally takes place after the foil is bonded to the substrate and before the photo resist is deposited on the foil's outer surface. This step is completely eliminated with this invention. This is made possible because the exposed surface of the laminate of the present invention (either the treated smooth or untreated matte) has  
25 sufficient topography or texture to allow for the adhesion of the photo resist without requiring the removal of the antioxidation treatment. Subsequent benefits of the elimination of this scrubbing process will be discussed at the inspection step. It is important to note that the elimination of this step is a benefit in two separate situations. The first situation is the multi-layer situation in which the

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etched foil will be subsequently relaminated to form an inner foil layer. The other situation is when the etched foil is a foil cap, that is, it will be left to form the outer layer of the finished circuit board. This other situation applies to all three types of PCB's; multi-layer, double-layer, and single-layer.

5 From this point through the inspection process, there is one design advantage which has been noted in certain situations. In "double-treat" foil, the surface texture created by the adhesion enhancing plating process on the smooth side sometimes acts to degrade the resolution which can be consistently achieved in the chemical etching process. This degradation of resolution would be even  
10 more serious if the circuit formation were done on a so treated matte side. Thus, in the present invention, production quality of higher resolution circuit patterns is increased when the photo resist is laminated to the untreated matte surface of the foil. At the inner layer inspection operation, the number of false call outs by the AOI equipment using reflective technology will be greatly reduced since the metal  
15 surface will not oxidize as readily as in current industry practices. As the number of false call outs is reduced, the number of escapes by human verifiers will decrease as they will have less call outs to verify thus allowing them to concentrate on finding functional defects. Also, this benefit will allow PCB shops to experience added flexibility in scheduling and should reduce cycle time as well.

20 Another step in which the foil of the present invention offers advantage is in the elimination of the pre-oxidizing microetch and associated rinses. Conventionally, after the circuit pattern is etched through the shiny side of the foil, the shiny surface must be partially etched to give it sufficient texture to form a foundation for the subsequent oxidizing step. The untreated matte side has  
25 sufficient texture to allow oxidizing without need for the microetch and associated rinses, while the treated shiny side out does not require the oxidizing process, because of the treatment.

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Another step in which the foil of the present invention offers advantage is the oxidizing step which is used in "single-treat" foil to prepare the originally shiny-side-out circuit pattern for subsequent bonding to another layer of prepreg or substrate. Either outer face of the foil of the present invention has been found, even without oxidizing to have sufficient adhesion properties to satisfy all but the most extreme specifications. Thus, there are applications where the oxidizing step can be eliminated.

In general, however, the oxidizing process would still be employed by PCB manufacturers who employ the foil of the invention, but several distinct benefits are achieved by the present invention. The first advantage is the complete elimination of the microetch bath and the rinse baths (typically two) associated with this microetch bath, as mentioned above. This results in the reduction of the volume of waste liquid and a reduction in the generation of hazardous waste.

The second advantage is the reduction of the amount of oxide crystal formation required to achieve bond strength equivalent to current industry practices and requirements. This results directly in lower chemical, material, and production costs and improved cycle time.

If the PCB manufacturer chooses to continue to maintain current dwell time in the oxide bath, adhesion improvements of greater than 40% have been achieved during experimentation with the present method. This essentially means that the overall reliability of the completed printed circuit board will be improved by over 40% in regards to delamination at the oxide/prepreg interface.

If the PCB manufacturer chooses to keep the adhesion strength between the oxide and the relamination prepreg at existing levels, experiments have shown a reduction in dwell time of 40% and a chemical consumption reduction of over 50%. Reduced costs and faster cycle times will yield results equal to current methods.

Another important advantage of the present invention when compared to

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the "double-treat" product results from the economic waste involved when a large amount of the adhesion enhancing plating on the shiny side is etched away in the circuit formation process. In the present process, even if oxidizing is necessary, it only occurs on the remaining circuit traces so that there is less waste of  
5 expensive surface treatment based on area treated.

Another advantage this product brings is the elimination of a post-dip reduction bath which follows the oxidation bath. Experiments have shown that the need for this chemical reduction process is no longer necessary in order to prevent "pink ring". Due to the matte surface on which the oxide crystals are formed, the  
10 leaching of acid in subsequent PCB manufacturing steps, is prevented. The removal of this step is significant as it is extremely hazardous (the mixture of reducing agents and oxidizing agents is highly volatile) and costly.

Another advantage of the embodiments of the invention in which the matte side is inward facing and oxidation requirements are eliminated, is the avoidance  
15 of a phenomena called "pink ring". A basis for rejection of a multi-layer circuit board can be that, when the board, with plated-through holes, is dipped in weak (10%) HCl, the acid leaches, from the hole, into the oxide layer that shows through the substrate, dissolves the oxide and allows a ring of copper to show through the substrate. By eliminating the outward-facing oxide layer, this basis  
20 for rejection is eliminated.

The circuit board construction of the present invention has been found to have an additional advantage. A very important test of circuit board quality involves thermal cycling of the board until the board delaminates at one of the bond layers. Unexpectedly, the circuit boards employing the present invention  
25 were found to be more resistant to thermally-induced initial delamination than circuit boards of traditional construction. Upon investigation, it was determined that the bond between the oxidized drum-side of the foil and the resin can sometimes have a tendency to weakness, delamination and, therefore, board failure. Both sides of the foil of the present invention form uniform and highly

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reliable bonds with the resin. This uniformity tends to eliminate the "weak link" or "failure point" found in traditional circuit boards.

Another embodiment of the present invention involves a concept which is a variation of a tooling concept and process described in U.S. Patent 5,153,050, issued on October 6, 1992 to James A. Johnston. Simply stated, the Johnston concept involves temporarily adhering the drum-side or shinny-side of a sheet of conventional copper circuit-board foil to one or both sides of a disposable aluminum plate. The copper-aluminum (-copper) laminate would be assembled into a press lay-up or book, as end panels and separators (if both sides of the aluminum were foiled), in the formation of circuit boards. This tool structure would protect the drum-side of the copper foil from damage or contamination before and during the foil-to-resin lamination process. After the foil-to-resin lamination process is completed, the bond between the copper and aluminum is terminated and the aluminum is reused or discarded.

This concept can be combined with the basic concept of the present invention (single-treated-drum-side foil) to form a variation which offers some substantial and unexpected advantages.

20

Basically, this variation of the invention involves a component or tool for use in manufacturing articles such as printed circuit boards. The component is a temporary laminate constructed of one or more sheets of drum-side-treated copper foil mounted on a sheet of aluminum. The copper foil, which, in a finished printed circuit board, will constitute a functional element, has a drum-side, which has been subjected to an adhesion-promoting treatment, and a rough side, which has not been subject to the adhesion-promoting treatment. The sheet of aluminum constitutes a discardable or reusable element. Either surface (treated drum-side or untreated matte side) of each copper sheet can be bonded to the aluminum, depending on which embodiment of the basic invention is being used. The side of the copper foil not bonded to the aluminum will be bonded to the resin in the next step. The bonding agent which serves to join the surfaces of the copper and

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aluminum sheets together protects the interface from external contamination and damage and assures a substantially uncontaminated central zone inwardly of the edges of the sheets on one or both sides of the aluminum sheet. Very importantly, this temporary structure provides a very protective physical support for the foil.

5 This expedites the handling of very thin or otherwise very delicate conductive foils. For example, this tool would allow handling of foil that is far too thin to be handled effectively by conventional means. This improved handability would be particularly important in automated versions of the production of circuit boards. The ability to handle ultra-thin copper foil could significantly reduce the amount

10 of copper that must be etched away to form the circuit paths and therefore would significantly reduce the amount of hazardous waste which results from the etching process.

A component or tool described above is employed in a method of manufacturing a copper and resin laminate, either as simple one or two foil-layer

15 boards, as intermediate laminates, or as multi-layer boards. The process, set out in the flow chart in Fig. 22, begins with a group of pre-press steps, which can be performed in any of a number of sequences. These pre-press steps are 41) forming a tool sheet having a first surface, 42) forming a sheet of copper having a drum-side and a rough side, 43) subjecting the drum-side of the copper foil to

20 an adhesion-promoting treatment, but not subjecting the rough side to an adhesion-promoting treatment, and 44) reversibly bonding one of the sides of the copper foil to one of the sides of the tool sheet to form a copper-clad tool.

Following the pre-press steps, the press steps are 45) positioning the copper foil, which is on the copper-clad tool, in contact with a resin layer in a laminating

25 press, to form a stack of layers, and 46) applying laminating conditions to the copper-clad tool and resin layer to bond the copper foil to the resin layer. Following the press steps, the post-press step 47 involves terminating the bond between the tool sheet and the copper foil and separating the tool sheet from the copper foil, which is now laminated to the resin.

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FIGS. 23-44 are diagrammatic sectional views of various foil-tool combinations and the steps in various processes involved in this variation of this invention.

FIG. 23 shows cross-sectional view of a single-sided tool 50 of the present invention. The tool is preferably a rectangular, rigid sheet or plate of aluminum 51. The conductive foil 52, preferably of copper, has a smooth or "drum-side" side 53 and a matte or rough side 54. The smooth side 53 is treated by plating, typically, with copper-zinc particles, to form an adhesion enhancement layer 55. FIG. 22 shows a foil 52 with the rough side 54 toward the plate 51. Bonding agent or adhesive 56 reversibly bonds the foil 52 to the plate 51.

FIG. 24 shows a variation of the tool shown in FIG. 23, the variation being that the tool 60 in FIG. 24 has the treated drum-side of the foil toward the plate 61. The conductive foil 62, preferably of copper, has a smooth or "drum-side" side 63 and a matte or rough side 64. The smooth side 63 is treated by plating, typically, with copper-zinc particles, to form an adhesion enhancement layer 65. FIG. 24 shows a foil with the treated drum-side toward the tool. Bonding agent or adhesive 66 reversibly bonds the foil to the tool.

FIG. 25 shows cross-sectional view of a double-sided tool 70 of the present invention. The tool is preferably a rectangular, rigid sheet or plate of aluminum 71. The conductive foils 72' and 72'', preferably of copper, each have a smooth or "drum-side" side 73' and 73'', respectively, and a matte or rough side 74' and 74'', respectively. The smooth sides 73' and 73'' are treated by plating, typically, with copper-zinc particles, to form adhesion enhancement layers 75' and 75''. FIG. 25 shows the foils with the rough sides 74' and 74'' toward the plate 71. Bonding agent or adhesive 76' and 76'' reversibly bonds the foil to the tool.

FIG. 26 shows a variation of the tool shown in FIG. 25, the variation being that the tool 80 in FIG. 26 has the treated drum-sides of the foils toward the plate 81. The conductive foils 82' and 82'', preferably of copper, each have a

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smooth or "drum-side" side 83' and 83'', respectively, and a matte or rough side 84' and 84'', respectively. The smooth sides 83' and 83'' are treated by plating, typically, with copper-zinc particles, to form an adhesion enhancement layer 85' and 85''. FIG. 26 shows the foils with the treated drum-side toward the plate  
5 81. Bonding agent or adhesive 86' and 86'' reversibly bond the foil to the tool.

FIGS. 27-32 show a fourth embodiment of the process of the present invention. FIG. 27 shows a step in which the foil 110 is formed on a smooth surface 114. FIG. 28 shows a step in which the smooth side 111 of the foil 110 is treated with an adhesion enhancing plating 113. FIG. 28 shows the foil 110  
10 mounted on tool sheet 101 or plate, preferably of aluminum. The matte side 112 is placed against the tool sheet 101. FIG. 29 shows a step in which the treated smooth surface 111 of the foil 110 is bonded to a first surface 115 of a substrate 116. This is accomplished by placing the stack shown in FIG. 29 into a lamination press. Pressure is applied inwardly and perpendicular to the tool sheet 101 and  
15 substrate 116. Simultaneously, heat is applied. Although FIG. 29 shows a very simple stack, those skilled in the art of laminate or circuit board manufacture will understand that this is diagrammatic of a more practical stack which would include numerous copper-resin interfaces and numerous tool-sheet-copper interfaces. Once the bond between the copper and the resin is formed, the bond between the tool  
20 sheet 101 and the copper 110 is terminated. The tool sheet or sheets 101 are removed from the copper and from the stack. The copper-resin laminate goes on to further processing, in earlier-recited ways. FIG. 30 shows a step in which the matte surface 112 of the foil 110 is coated with photo resist 117 without the need for a prior scrubbing process. FIG. 31 shows a step in which the matte surface  
25 112, from which the photo resist has been removed, is treated with an oxidizing process, to form an oxide layer 118, without the need for a prior microetch and rinse process. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, it would not need the oxidizing treatment and would be complete without it and without the next step. FIG. 32 shows a step in which  
30 a second substrate 119 is bonded to the oxidized matte side 112 of the foil 110.

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FIGS. 33-38 show a fifth embodiment of the process of the present invention. FIG. 33 shows a step in which the foil 120 is formed on a smooth surface 124. FIG. 34 shows a step in which the smooth side 121 of the foil 120 is treated with an adhesion enhancing plating 123. FIG. 34 shows the foil 120 mounted on tool sheet 102 or plate, preferably of aluminum. The matte side 122 is placed against the tool sheet 102. FIG. 35 shows a step in which the treated smooth surface 121 of the foil 120 is bonded to a first surface 125 of a substrate 126. This is accomplished by placing the stack shown in FIG. 35 into a lamination press. Pressure is applied inwardly and perpendicular to the tool sheet 102 and substrate 126. Simultaneously, heat is applied. Although FIG. 35 shows a very simple stack, those skilled in the art of laminate or circuit board manufacture will understand that this is diagrammatic of a more practical stack which would include numerous copper-resin interfaces and numerous tool-sheet-copper interfaces. Once the bond between the copper and the resin is formed, the bond between the tool sheet 102 and the copper 120 is terminated. The tool sheet or sheets 102 are removed from the copper 120 and from the stack. The copper-resin laminate goes on to further processing, in earlier-recited ways. FIG. 36 shows a step in which the matte surface 122 of the foil 120 is coated with photo resist 127 without the need for a prior scrubbing process. FIG. 37 shows a step in which the photo resist 127 has been removed from the matte surface 122. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, you would not have a subsequent relamination over this layer, so the next step would not be necessary. FIG. 38 shows a step in which a second substrate 129 is bonded to the untreated and unoxidized matte side 122 of the foil 120.

FIGS. 39-44 show a sixth embodiment of the process of the present invention. FIG. 39 shows a step in which the foil 130 is formed on a smooth surface 134. FIG. 40 shows a step in which the smooth side 131 of the foil 130 is treated with an adhesion enhancing plating 133. FIG. 40 shows the foil 130 mounted on tool sheet 103 or plate, preferably of aluminum. The treated smooth side 131 is placed against the tool sheet 103. FIG. 41 shows a step in which the

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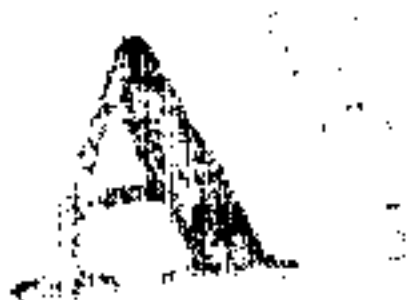
untreated matte surface 132 of the foil 130 is bonded to a first surface 135 of a substrate 136. This is accomplished by placing the stack shown in FIG. 41 into a lamination press. Pressure is applied inwardly and perpendicular to the tool sheet 103 and substrate 136. Simultaneously, heat is applied. Although FIG. 41 shows a very simple stack, those skilled in the art of laminate or circuit board manufacture will understand that this is diagrammatic of a more practical stack which would include numerous copper-resin interfaces and numerous tool-sheet-copper interfaces. Once the bond between the copper 130 and the resin 136 is formed, the bond between the tool sheet 103 and the copper 130 is terminated. The tool sheet or sheets 103 are removed from the copper 130 and from the stack. The copper-resin laminate goes on to further processing, in earlier-recited ways. FIG. 42 shows a step in which the treated smooth surface 131 of the foil 130 and plated layer 133 are coated with photo resist 137 without the need for a prior scrubbing process. FIG. 43 shows a step in which the photo resist 137 has been removed from the treated smooth surface 131. It will be understood by those skilled in the art that if this foil is a cap or outside foil layer, you would not have a subsequent relamination over this layer, so the next step would not be necessary. FIG. 44 shows a step in which a second substrate 139 is bonded to the treated smooth side 131 of the foil 130.

It is obvious that minor changes may be made in the form and construction of the invention without departing from the material spirit thereof. It is not, however, desired to confine the invention to the exact form herein shown and described, but it is desired to include all such as properly come within the scope claimed.

The invention having been thus described, what is claimed as new and desired to secure by Letters Patent is:

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

1. A method of forming a printed circuit board consisting of:  
depositing a quantity of an electrically conductive material onto a smooth forming surface to form a foil having a first smooth surface which forms against the forming surface, and a second matte surface which forms away from the forming surface,  
plating an adhesion promoting layer on said first surface,  
treating the plated foil with an oxidation retardant,  
bonding one of said plated first surface and said unplated second surface of said treated foil which carries said oxidation retardant to a first electrically insulative substrate, and forming a circuit pattern on the other of said first surface and said second surface of said treated foil which carries said oxidation retardant by the application and selective removal of a photo-resist material.
2. A method according to claim 1 and further comprising the step of bonding said other of said first surface and second surface to a second electrically insulative substrate.
3. A method according to claim 2 in which the matte surface from which the photo resist has been removed is treated with an oxidising process to form an oxide layer, and the second substrate is bonded to the oxidised matte side of the foil.
4. A method according to any one of claims 1 to 3 in which the foil is formed with the matte side having an  $R_z < 10.2$  microns, where  $R_z$  is the mean peak-to-valley height of the matte teeth.



5. A method according to any one of claims 1 to 4 which includes providing a tool sheet which constitutes a discardable element, bonding one of said plated first surface and said unplated second surface to the tool sheet to form a temporary laminate,

bonding the other of said plated first surface and said unplated second surface to the first electrically insulative substrate, and terminating the bond between the tool sheet and the foil and separating the tool sheet from the foil.

6. A method according to claim 5 wherein the tool sheet is aluminum.

7. A method according to any one of claims 1 to 6 wherein the foil is copper.

8. A method according to any one of claims 1 to 7 wherein the nominal dielectric thickness range of the first electrically insulative substrate is between 0.00019 of an inch and 0.2510 of an inch.

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Fig. 1

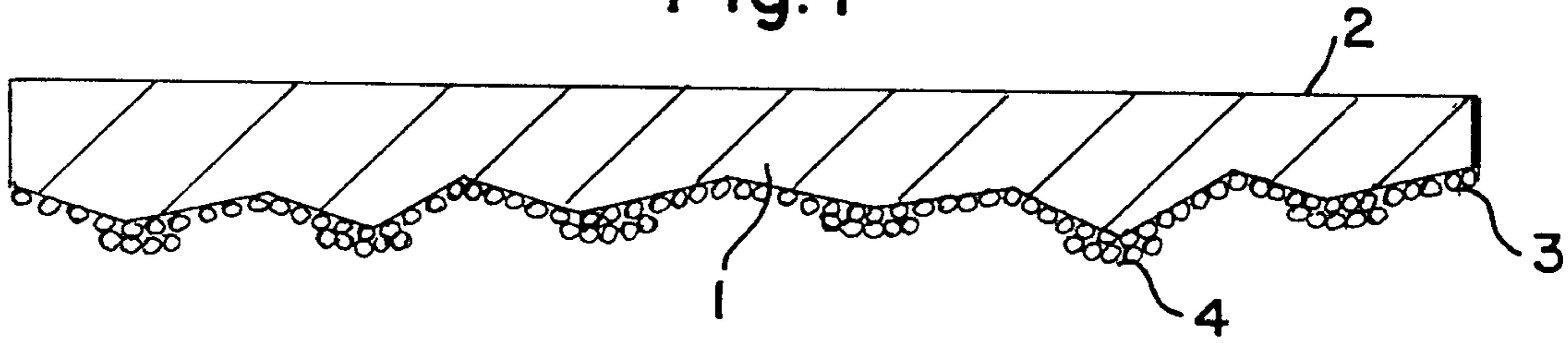


Fig. 2

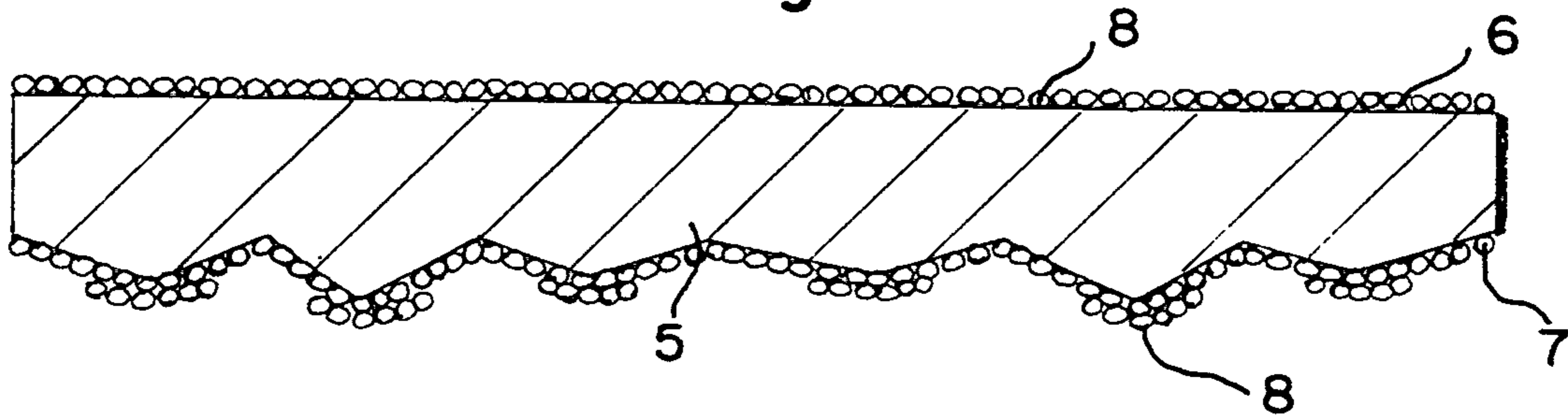
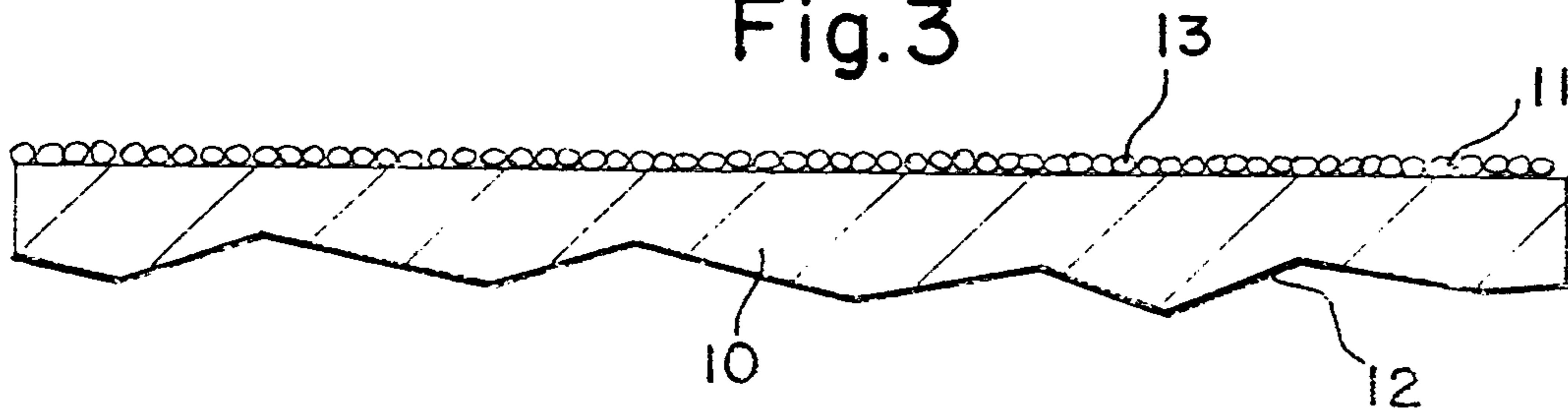
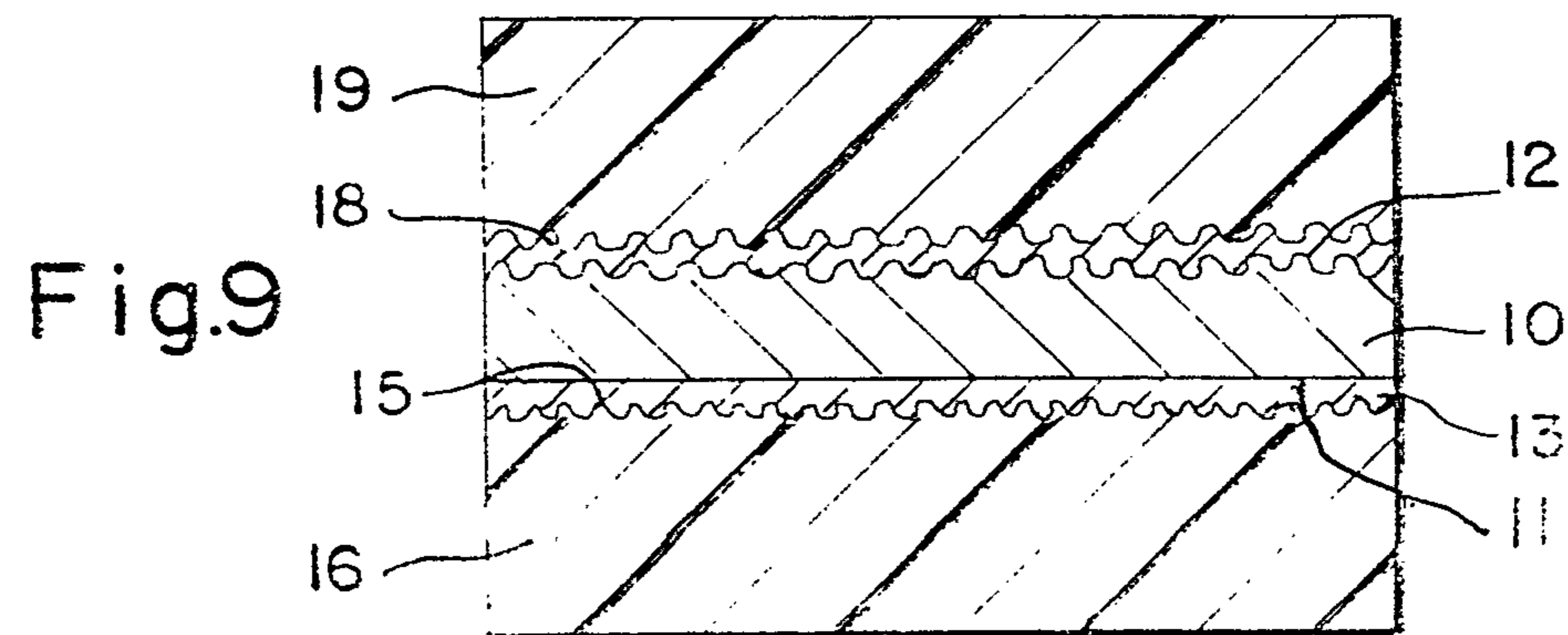
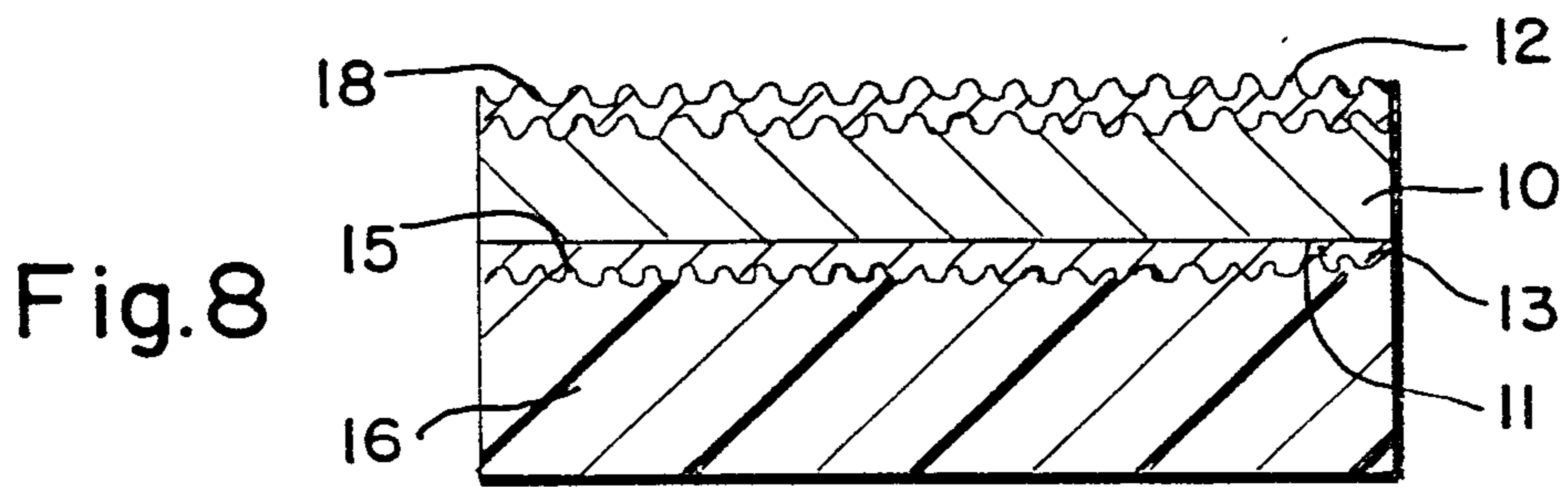
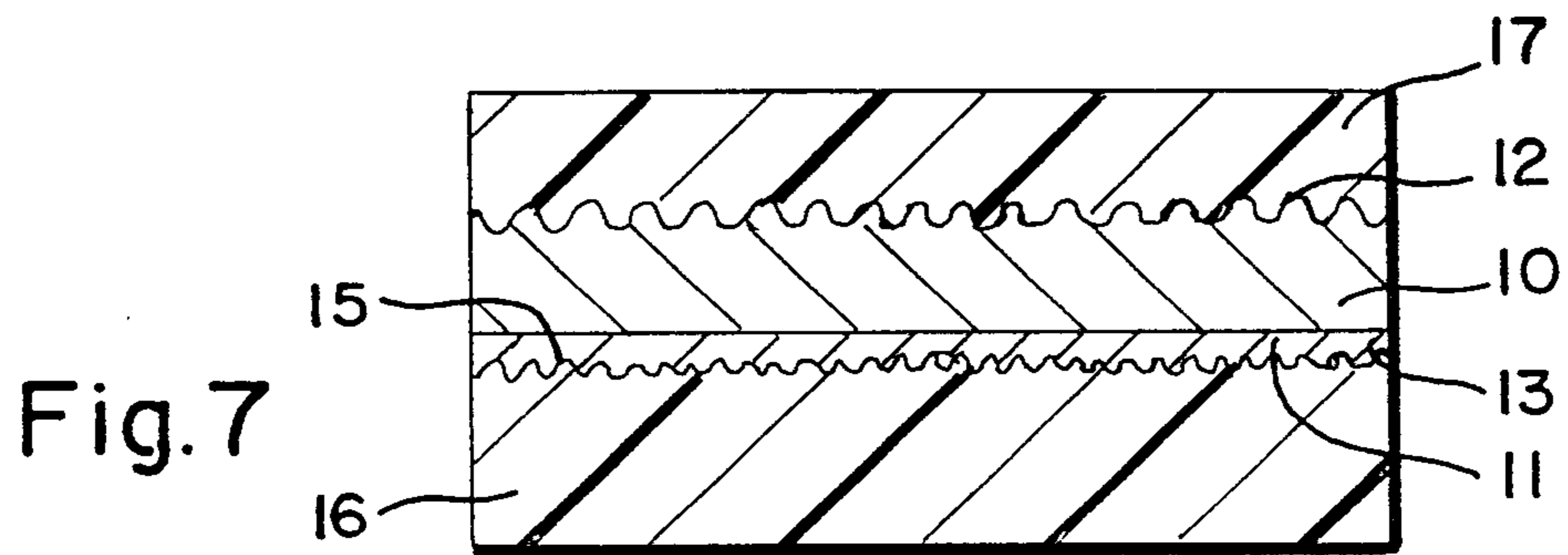
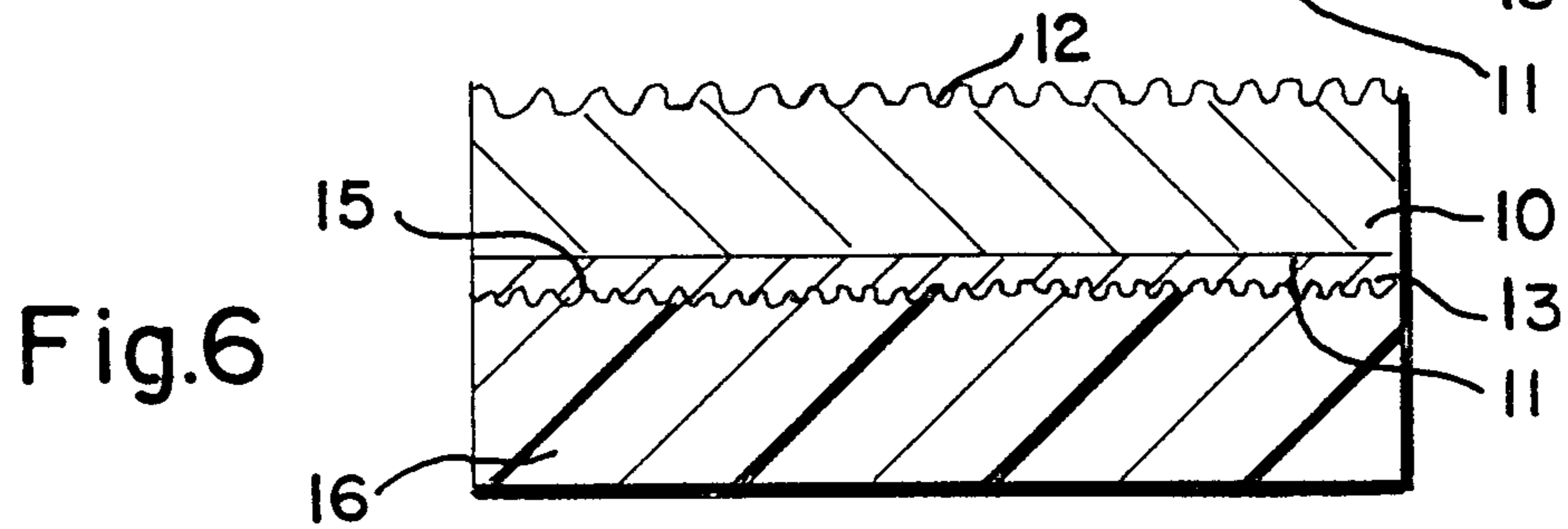
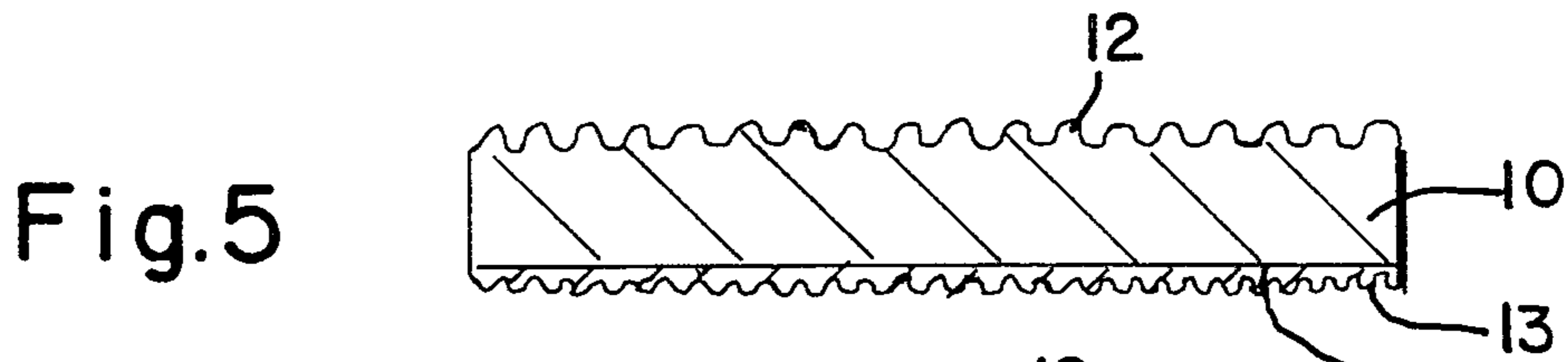
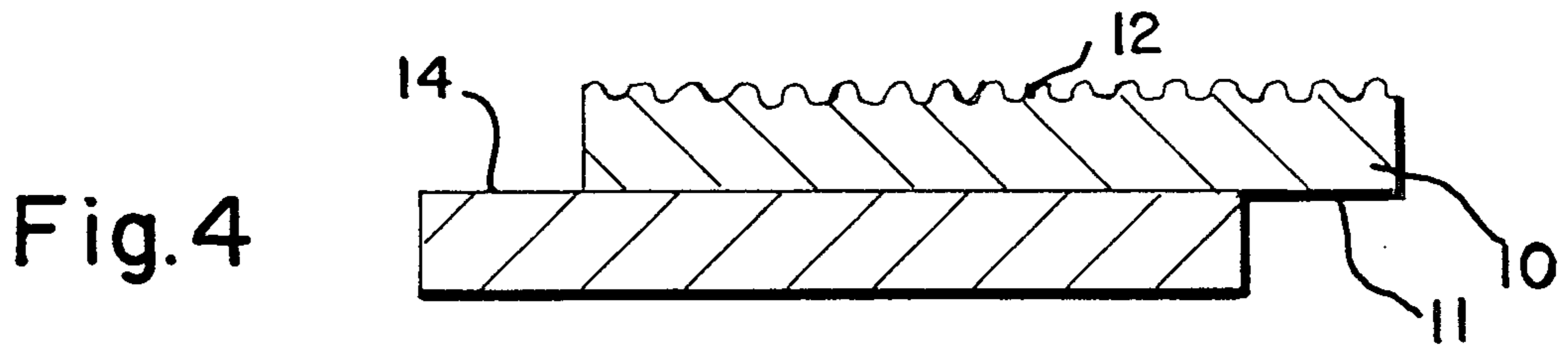
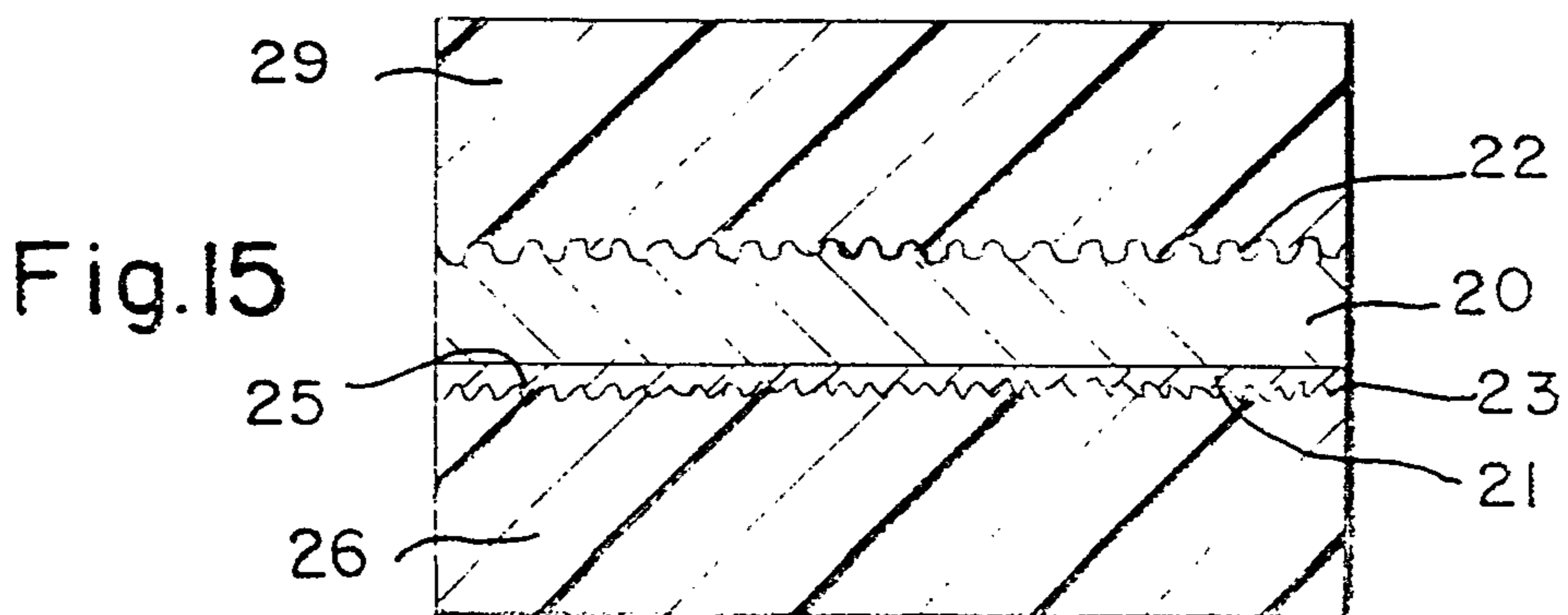
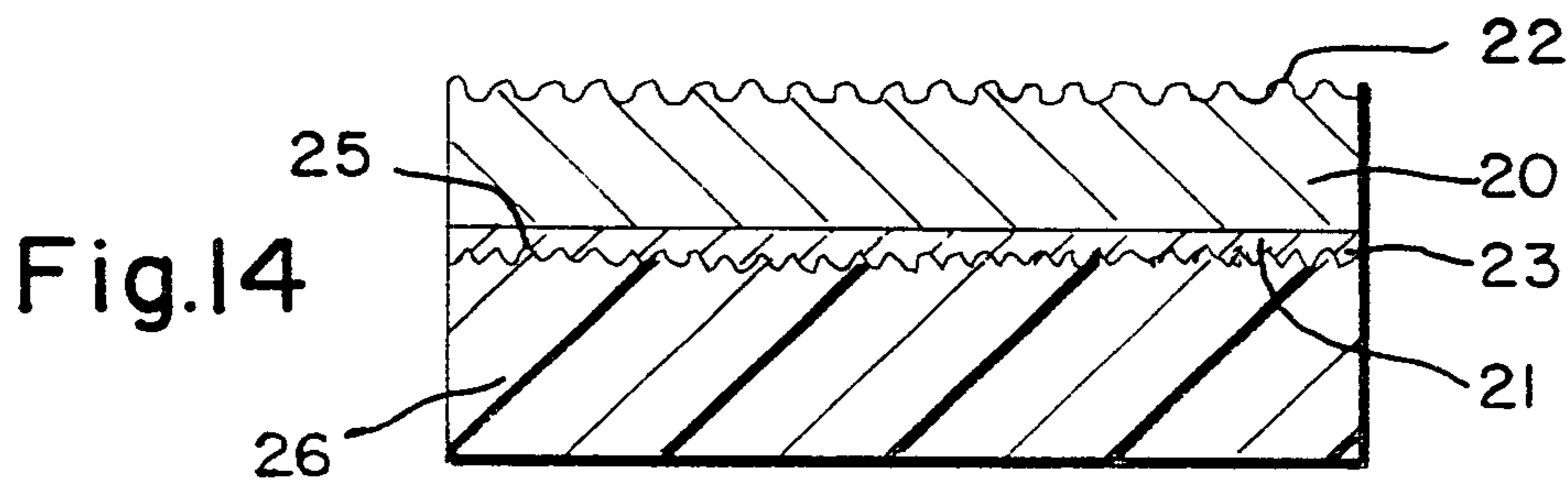
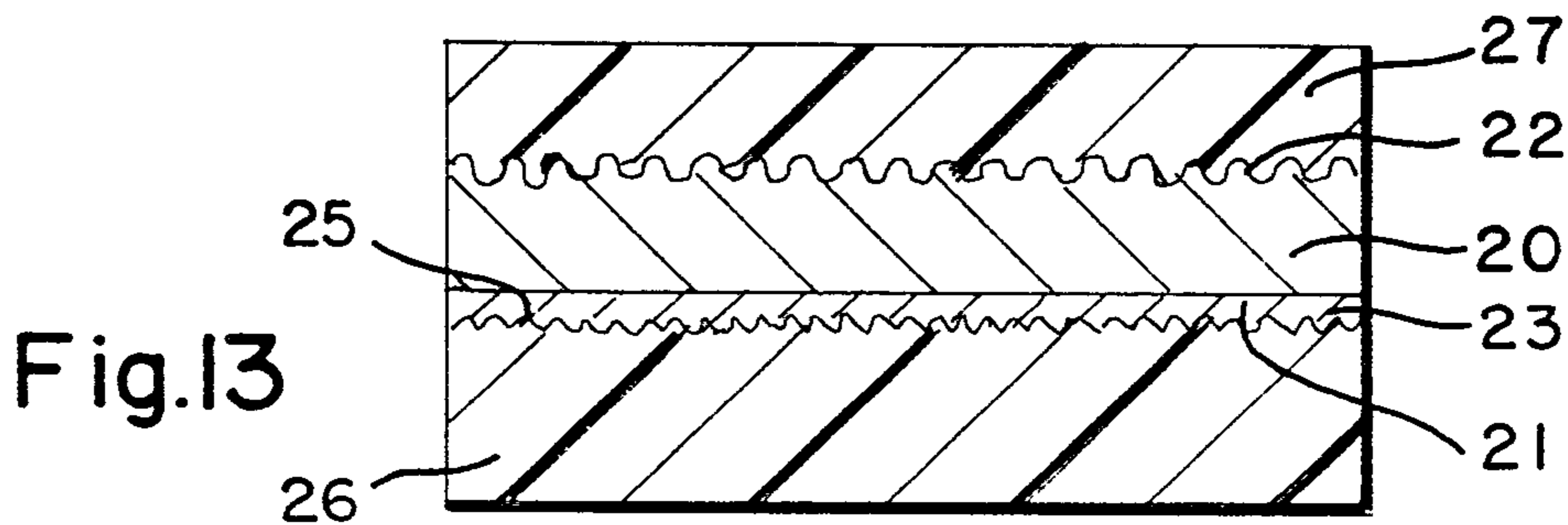
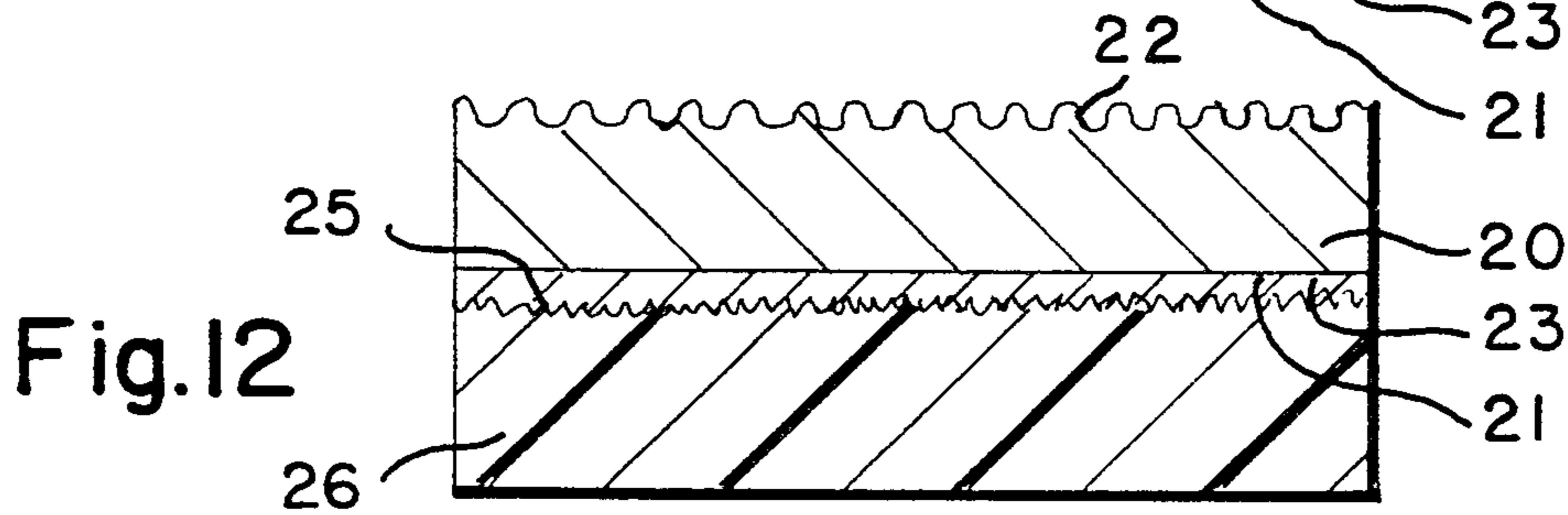
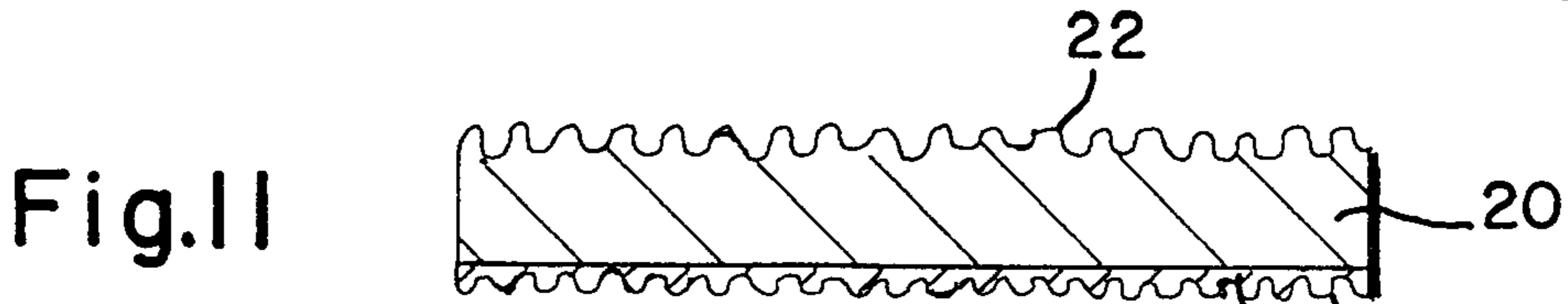
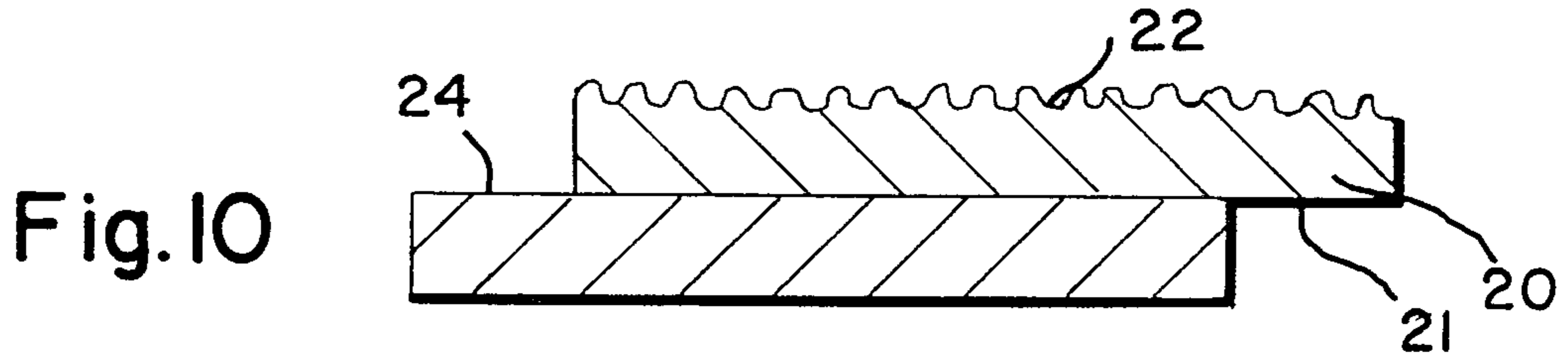
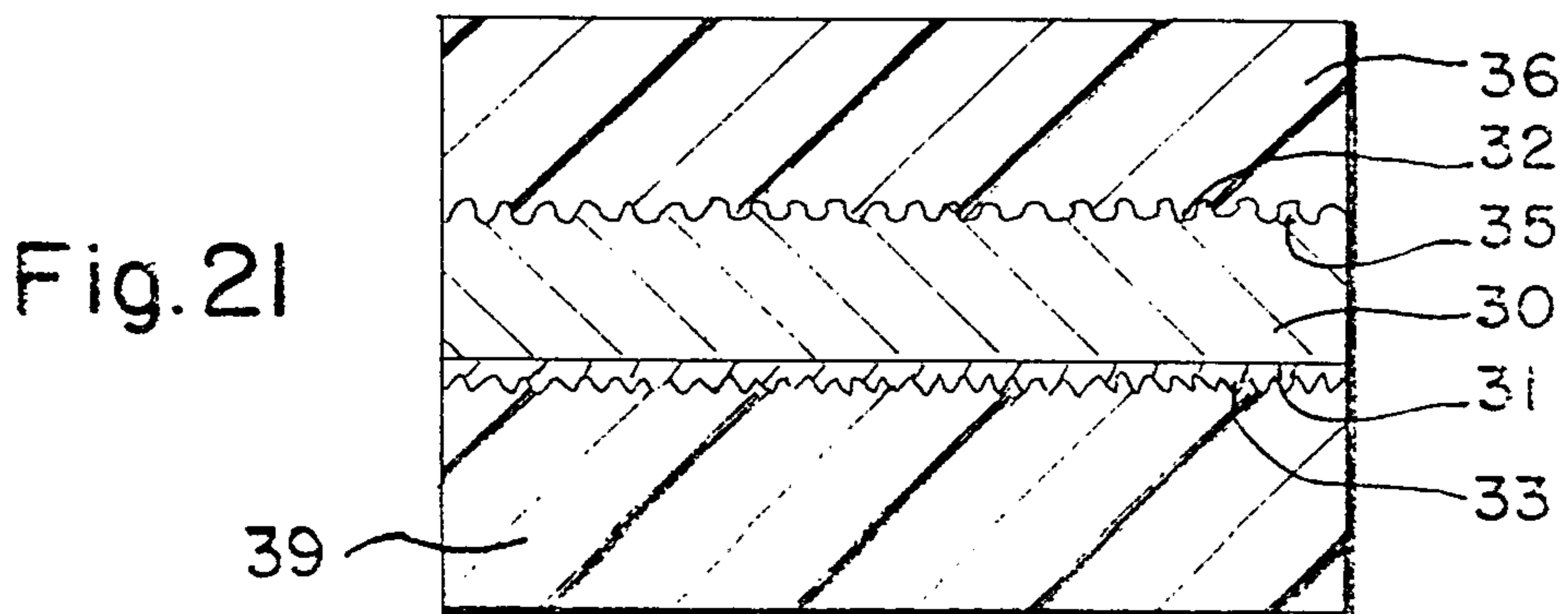
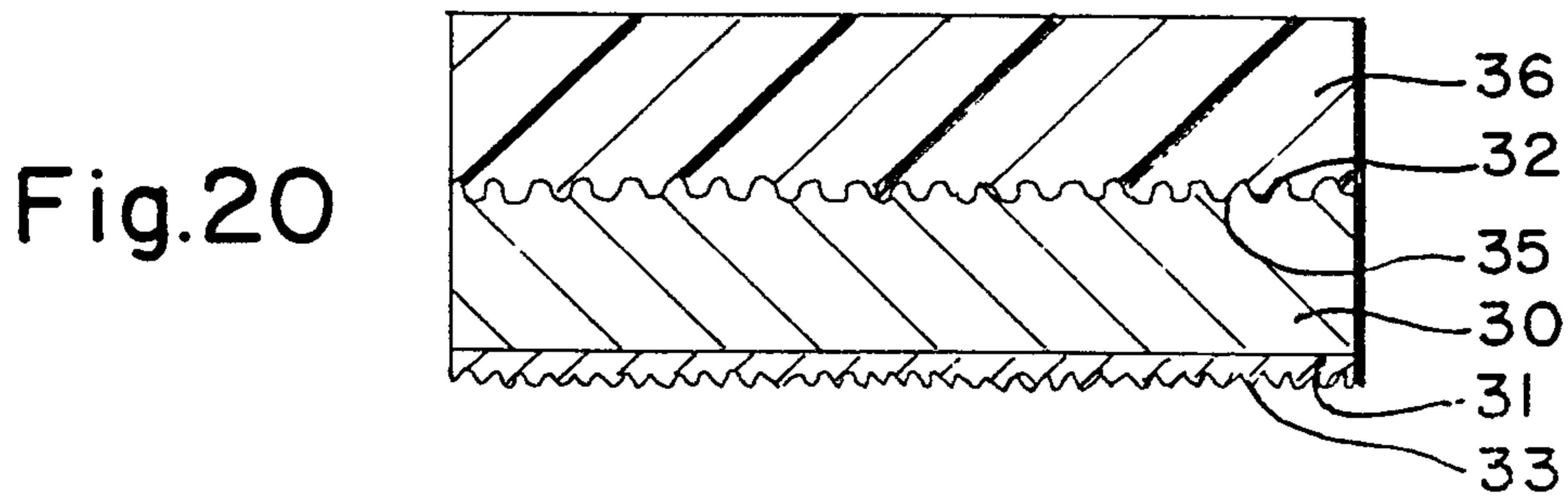
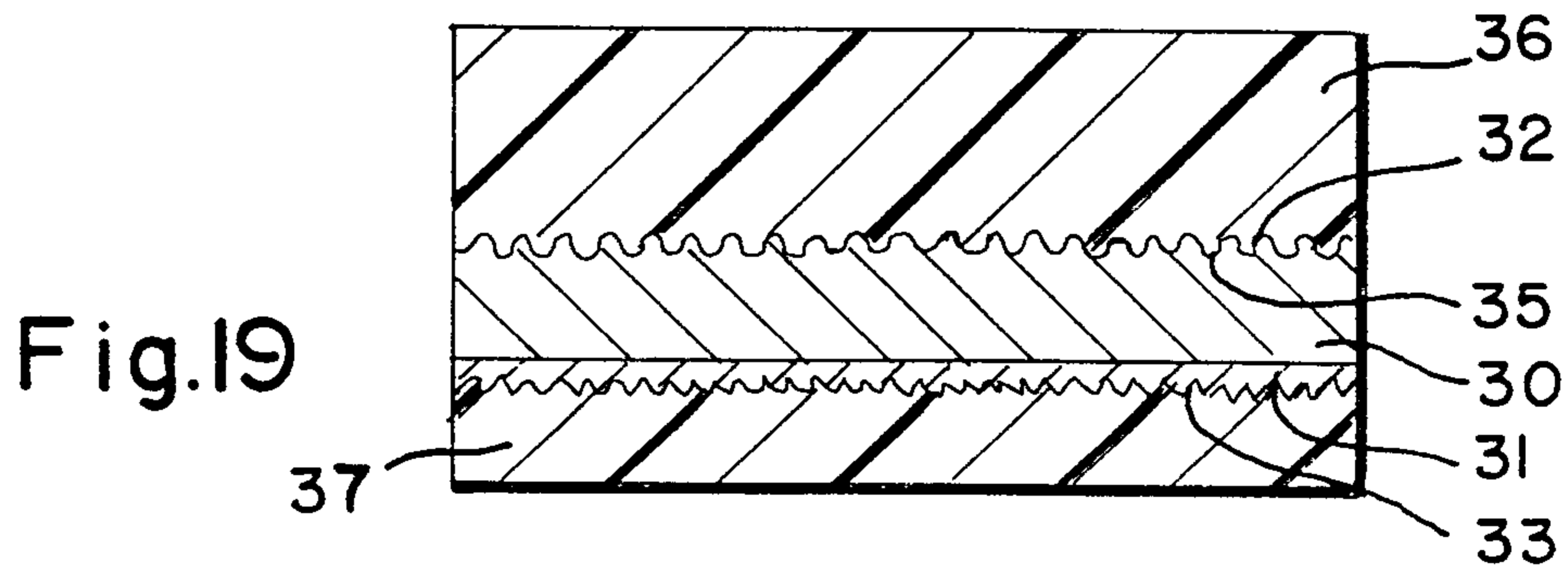
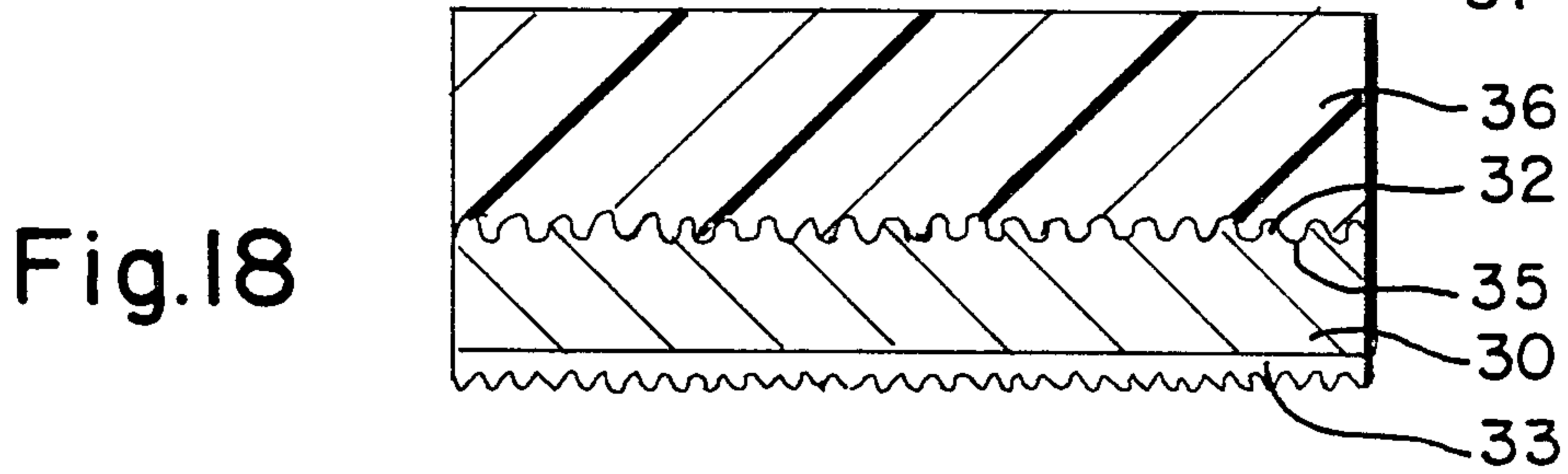
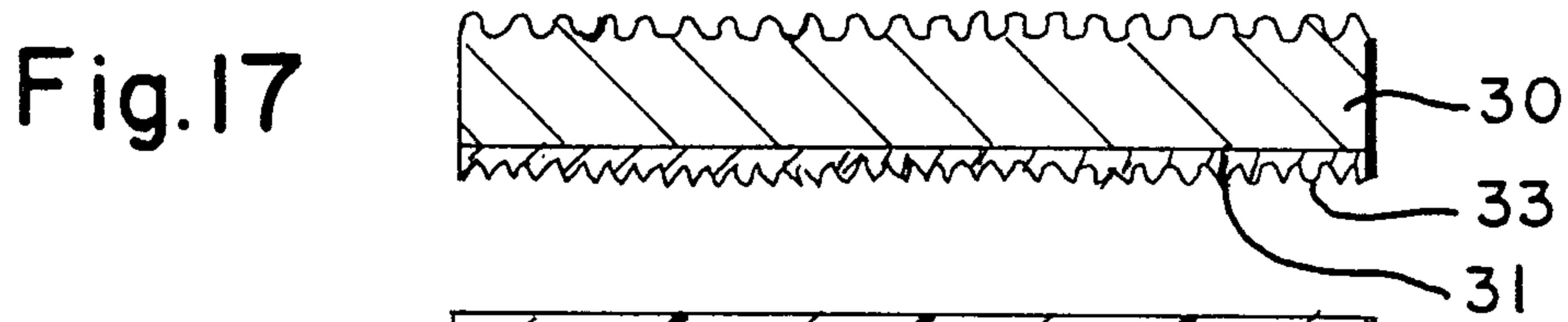
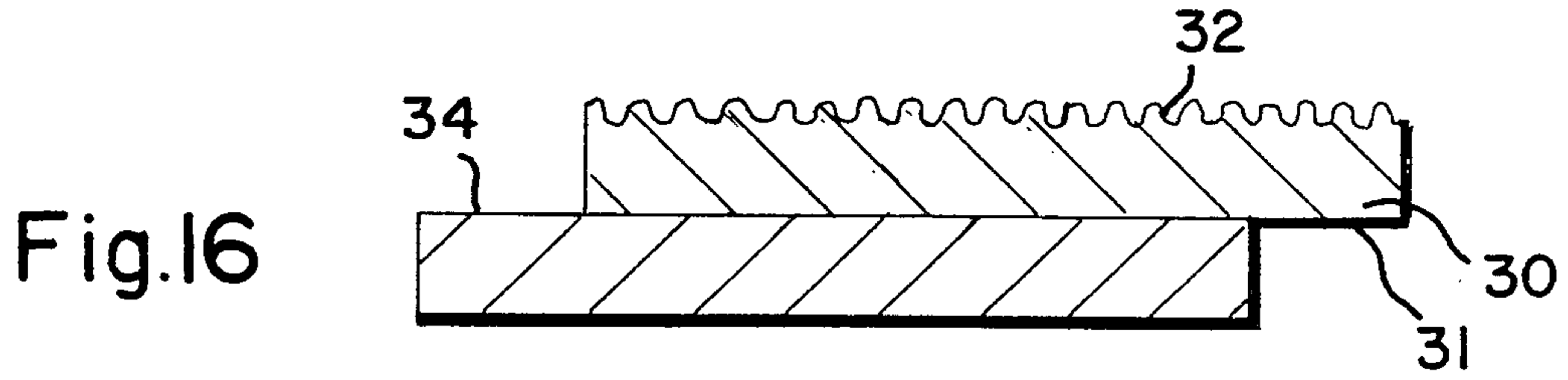


Fig. 3









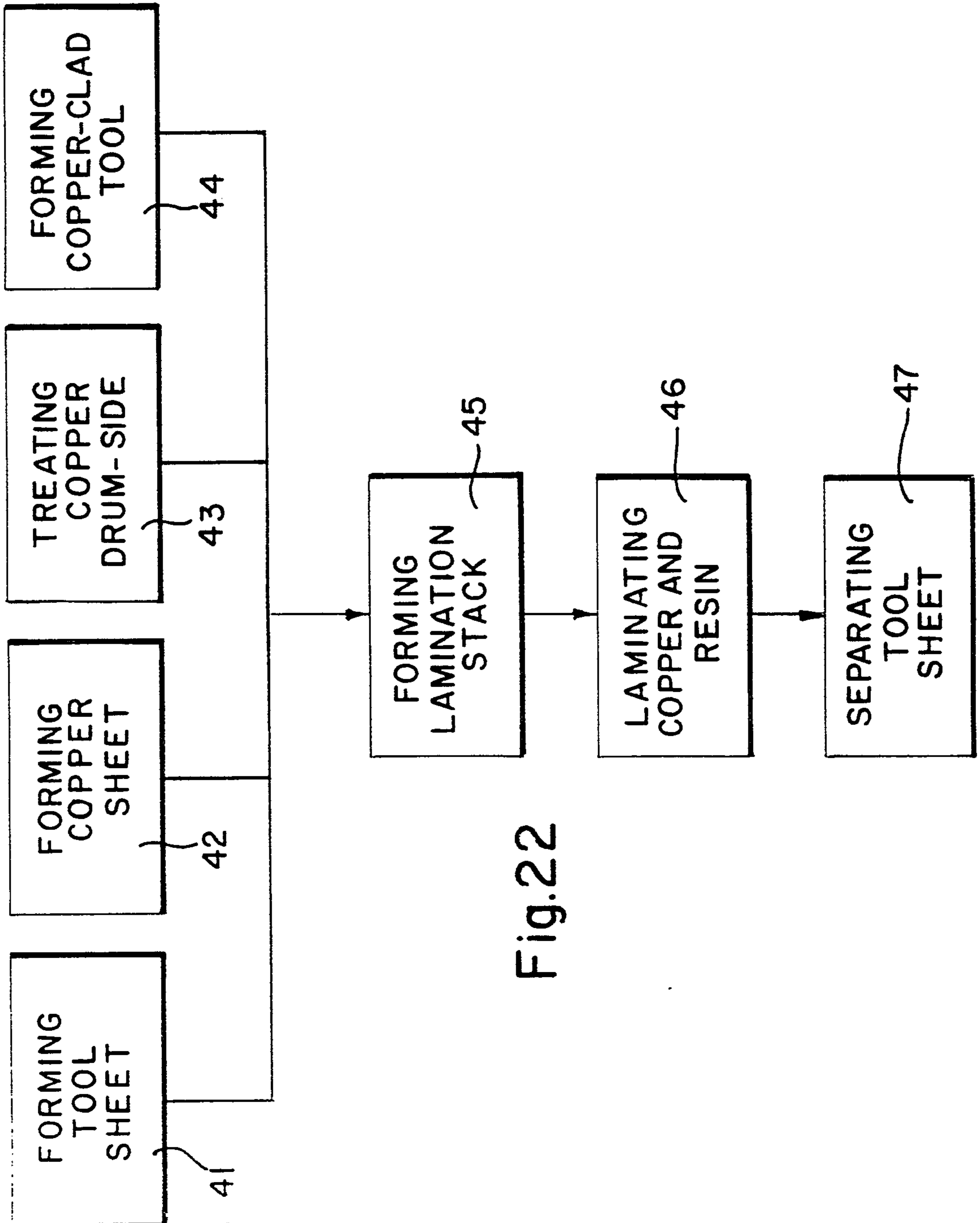


Fig.22

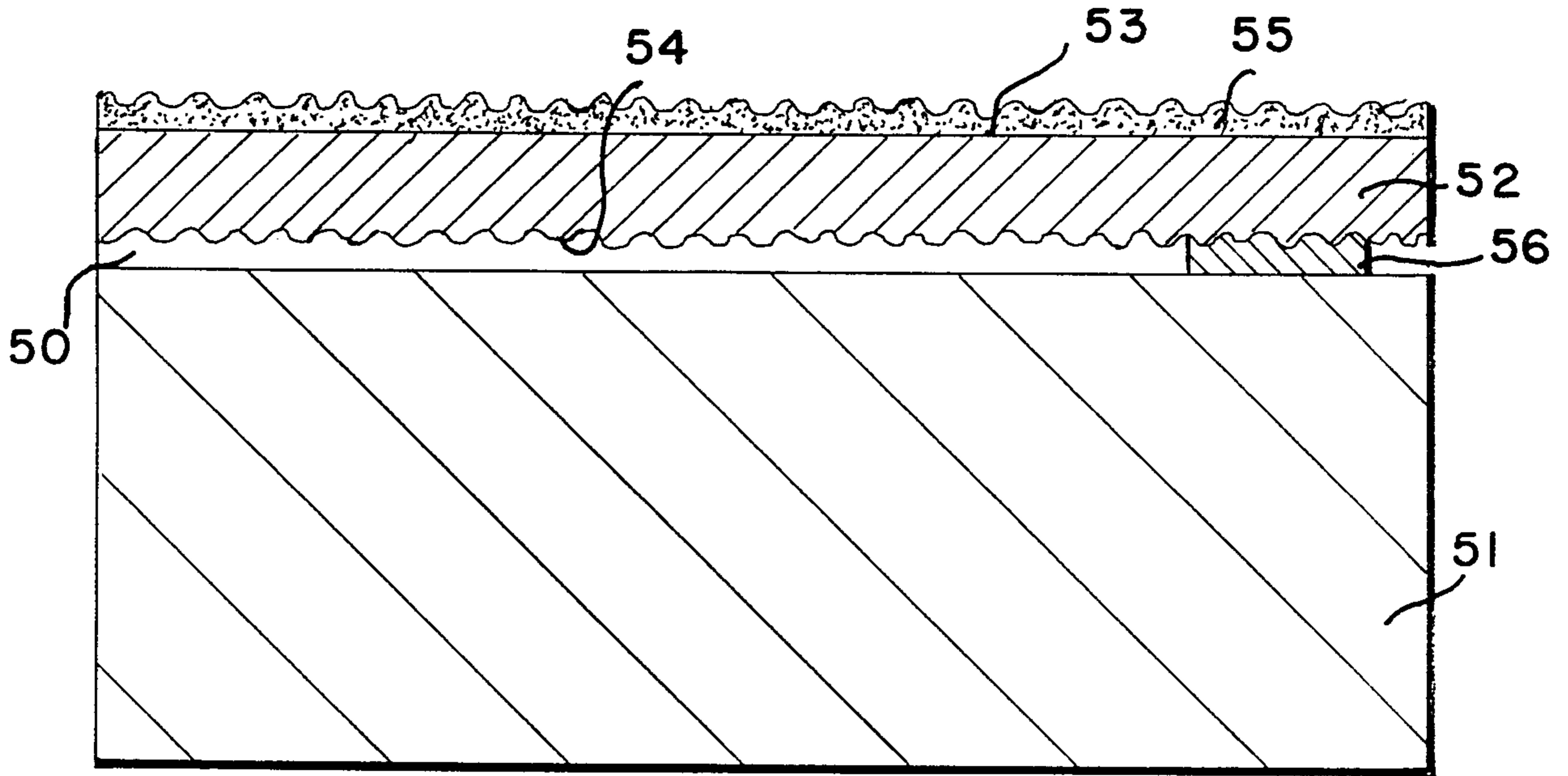


Fig.23

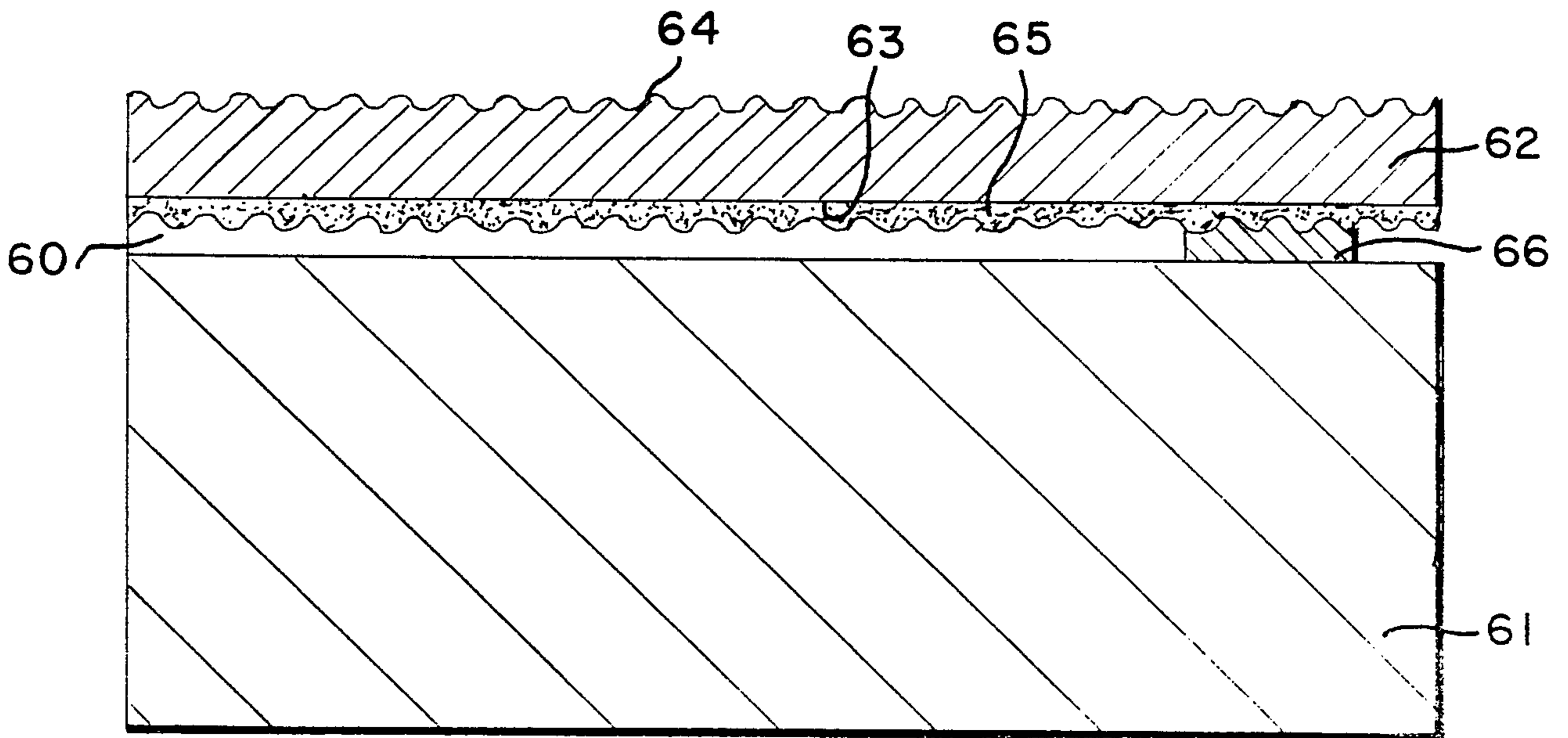
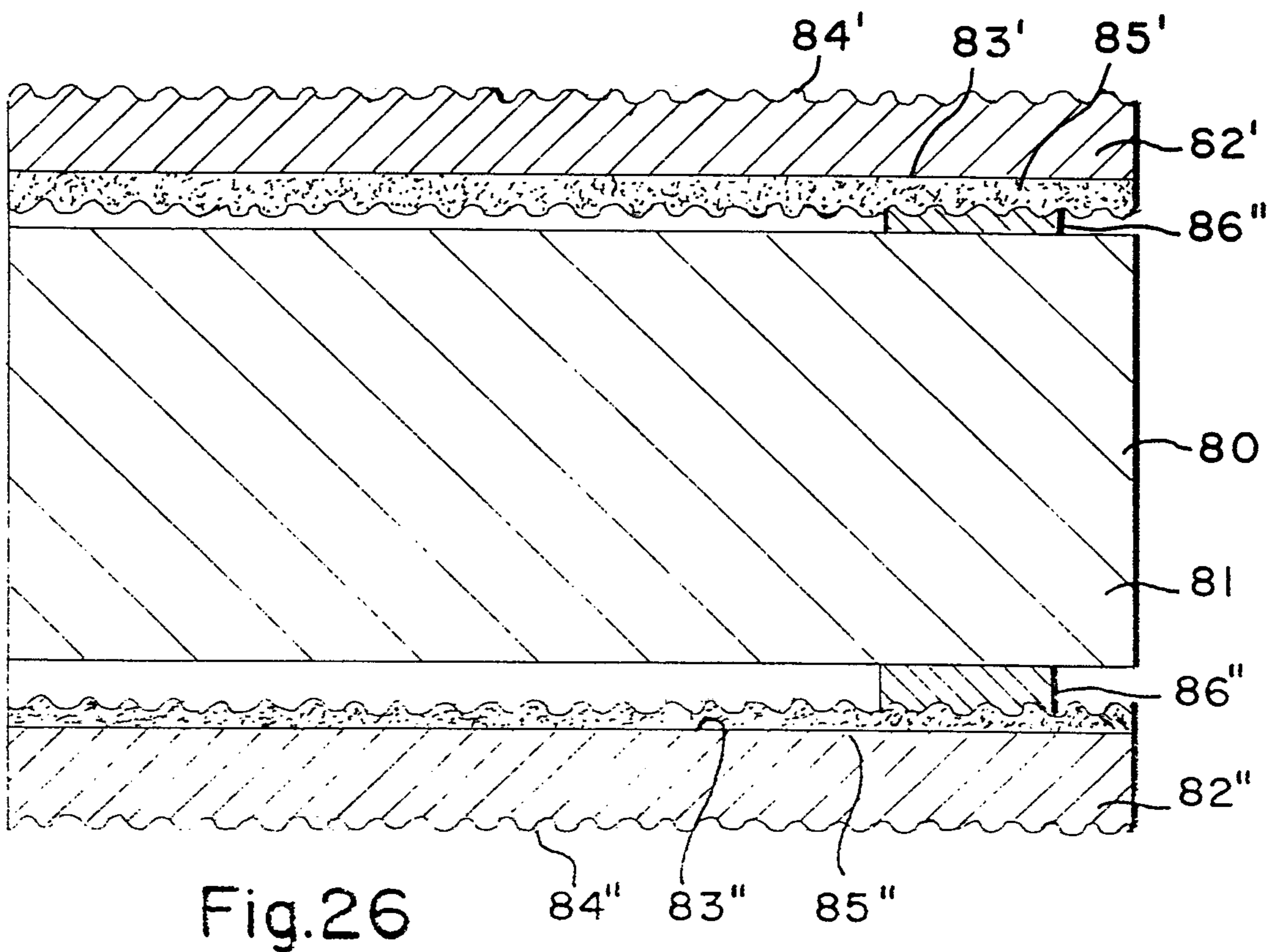
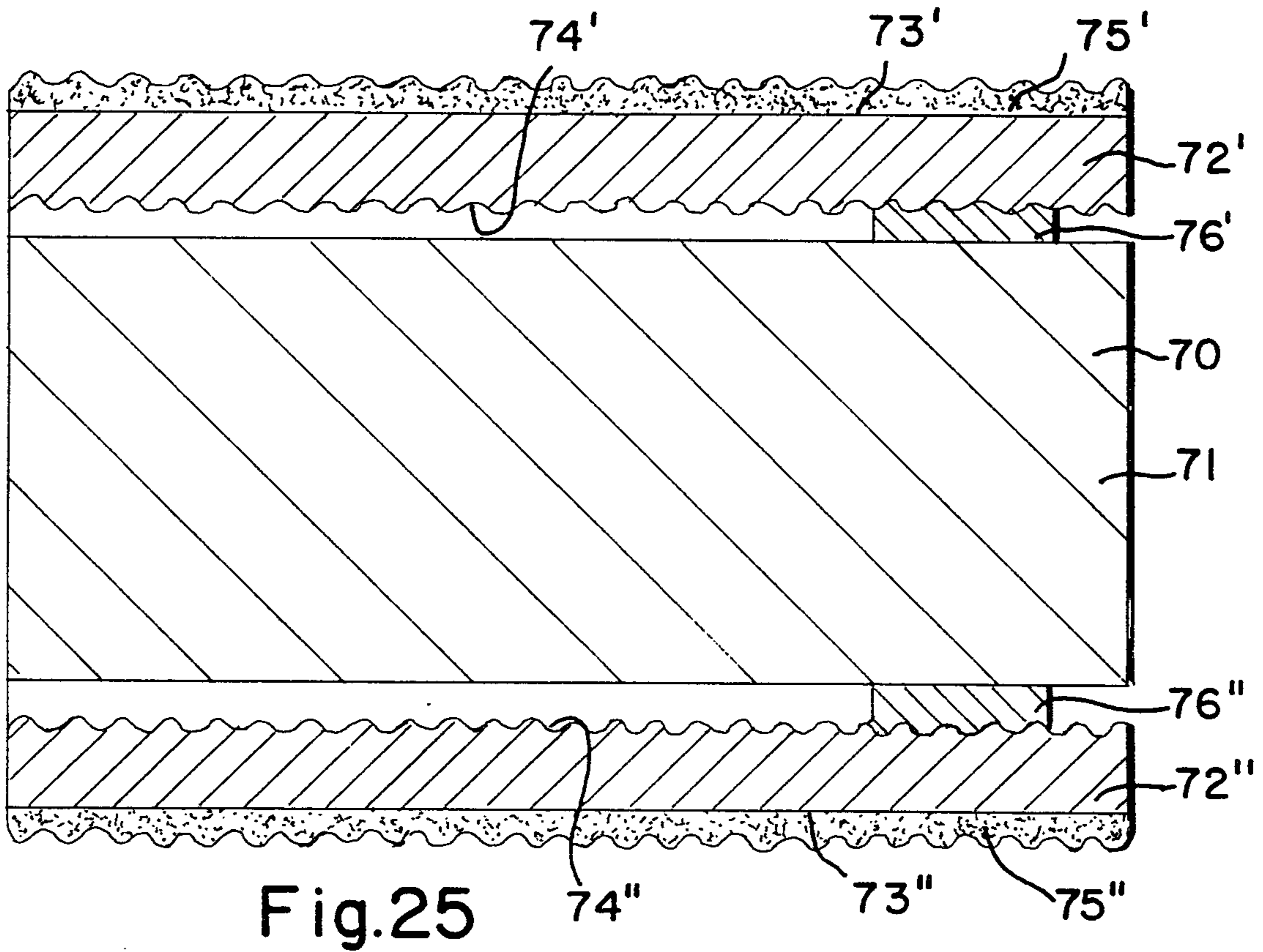
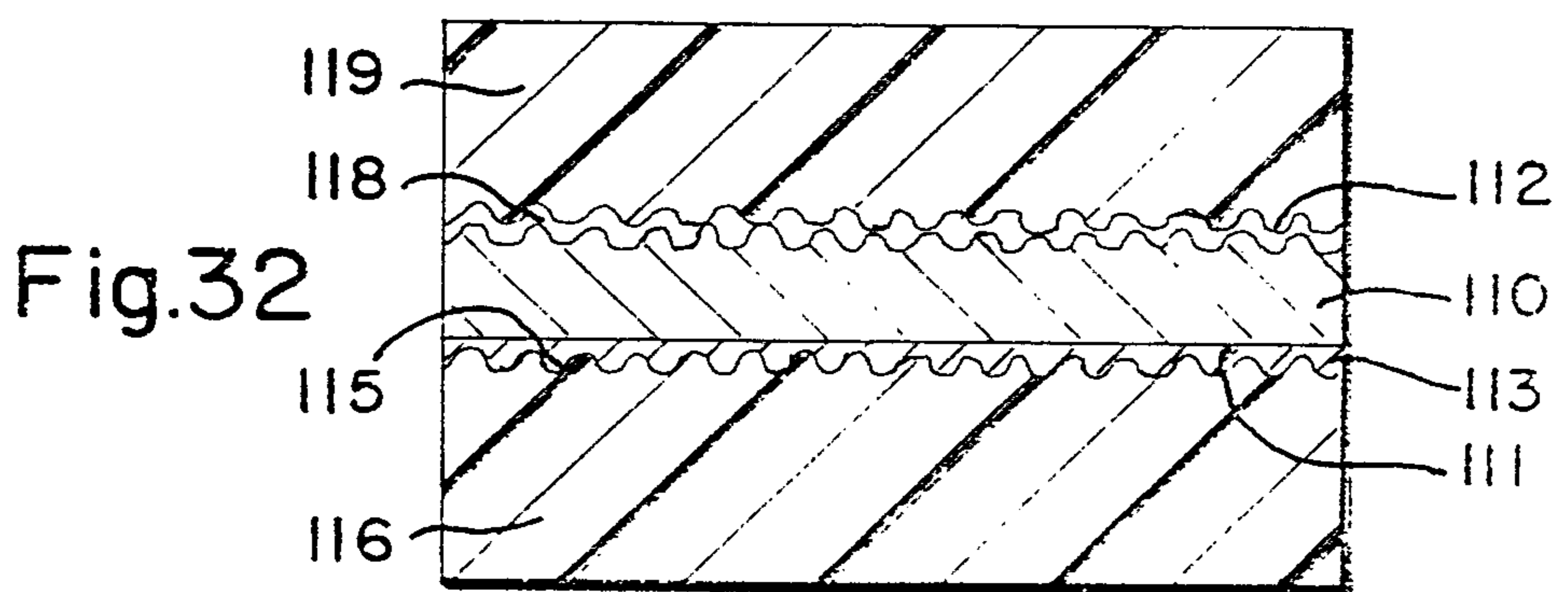
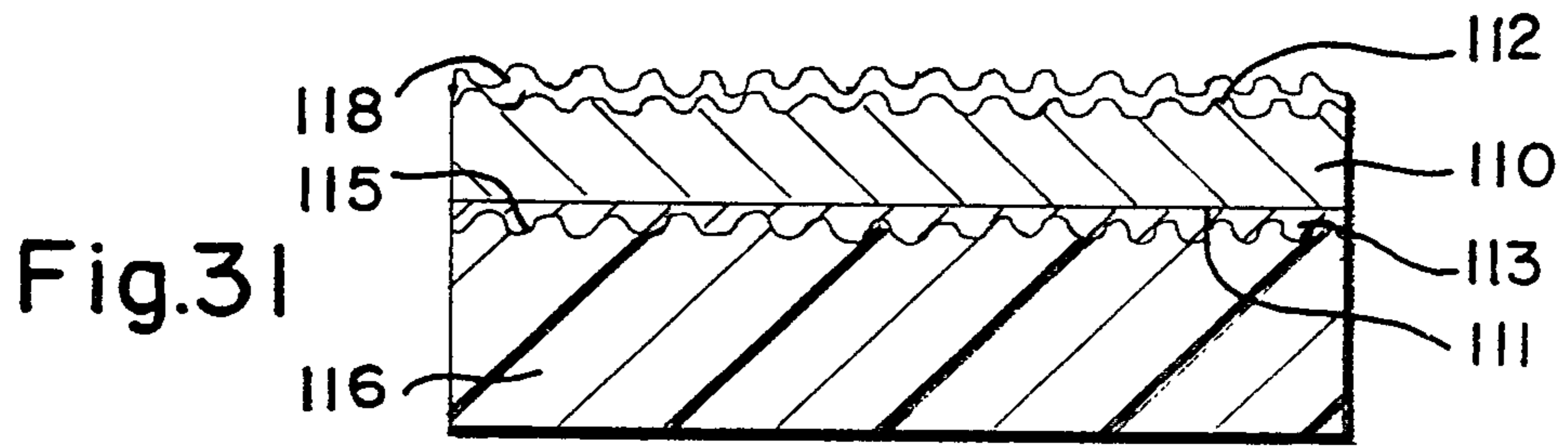
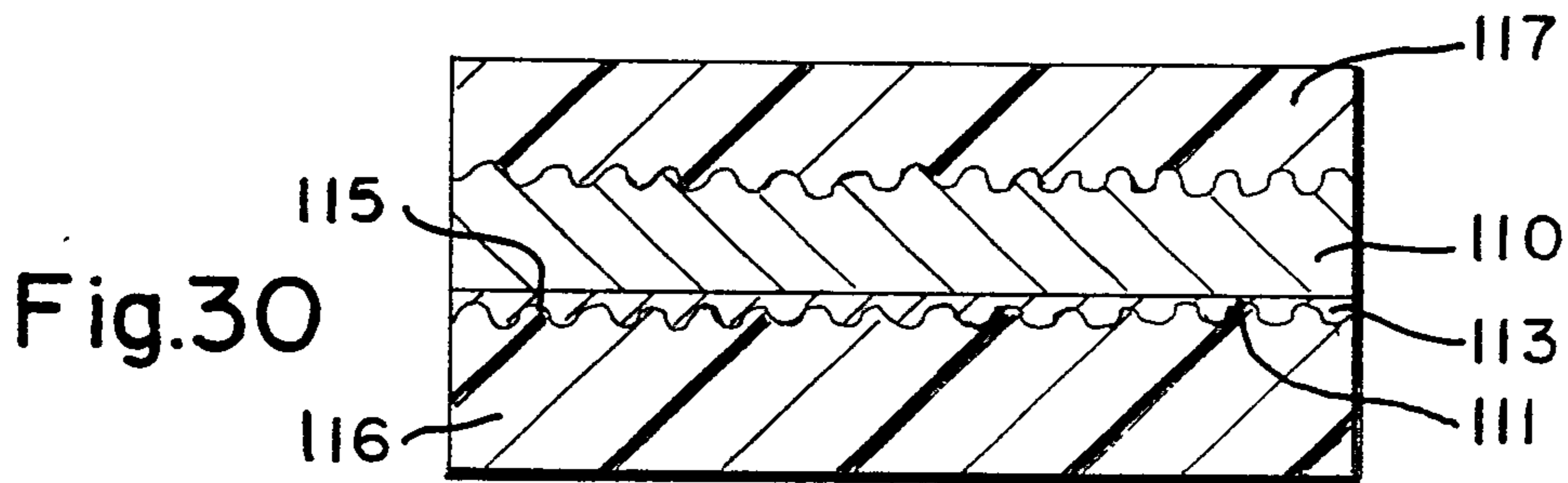
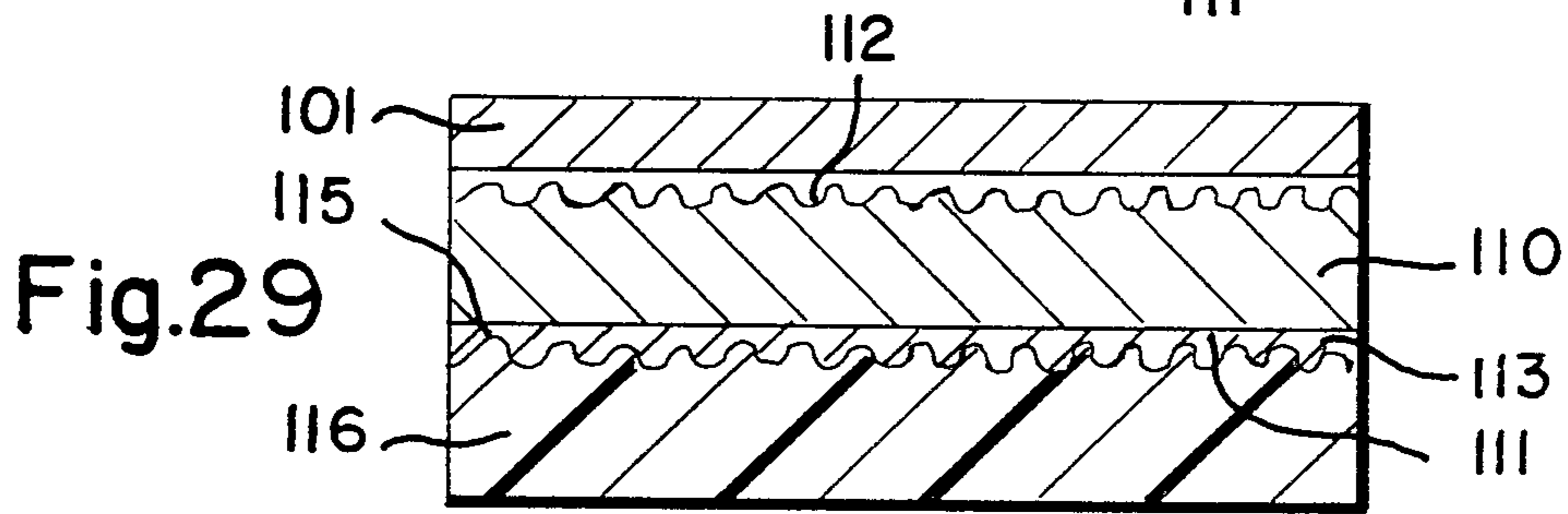
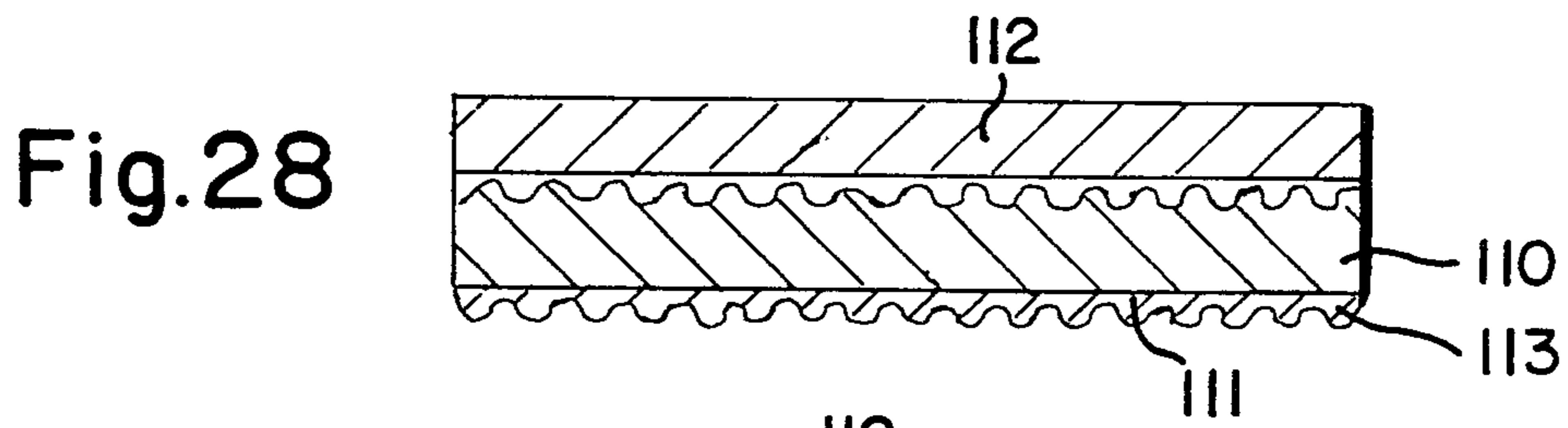
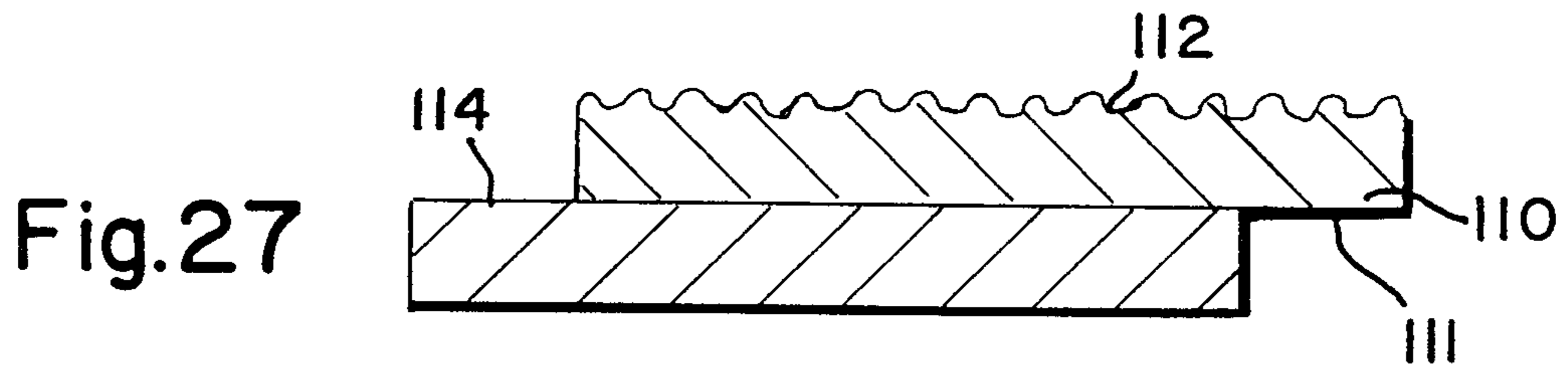


Fig.24





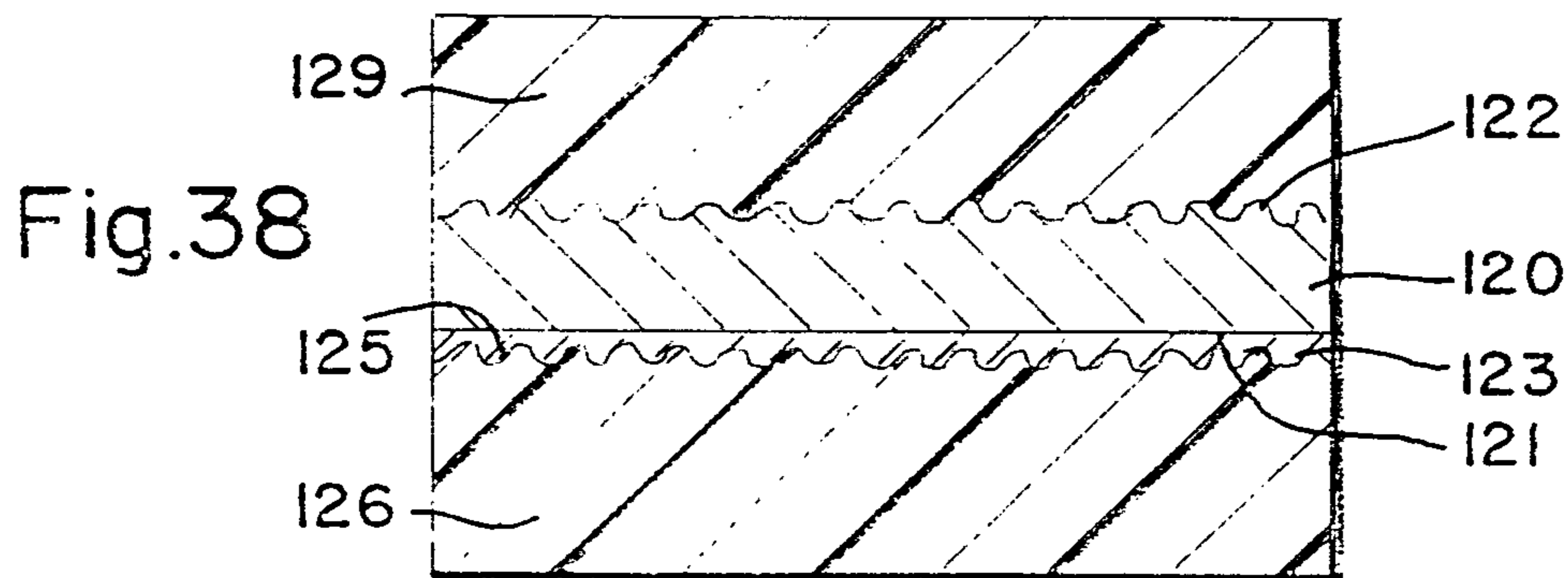
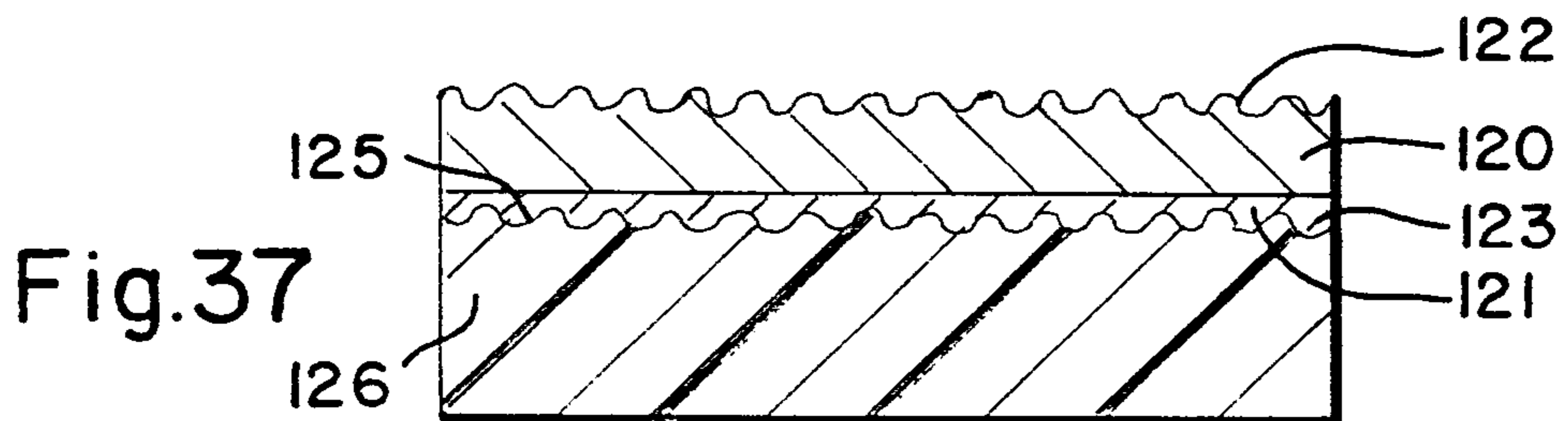
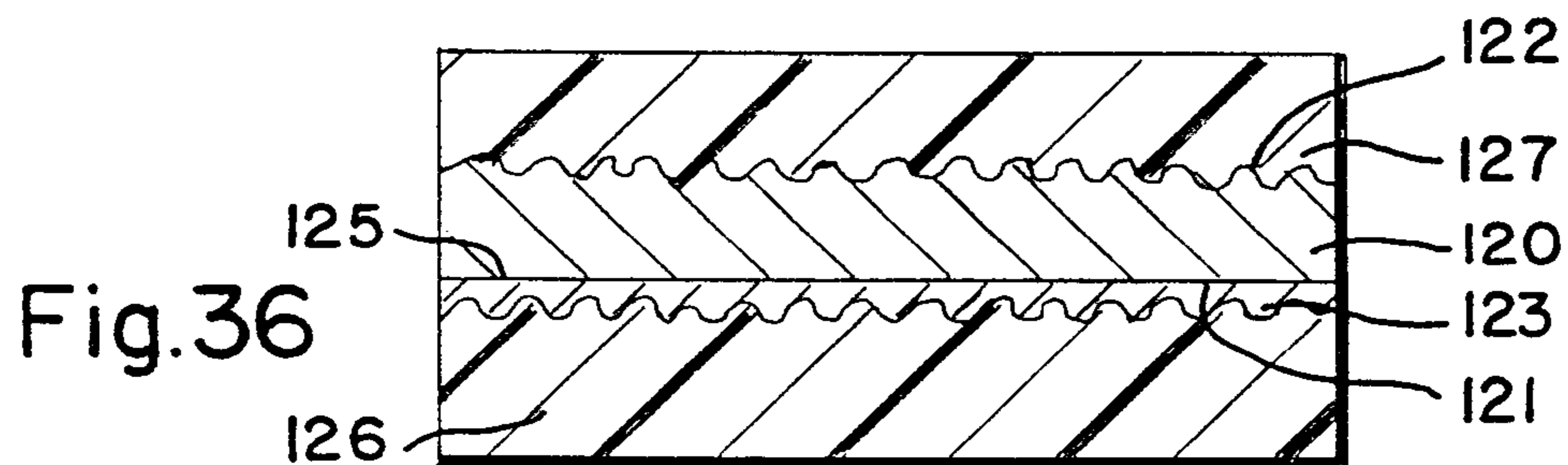
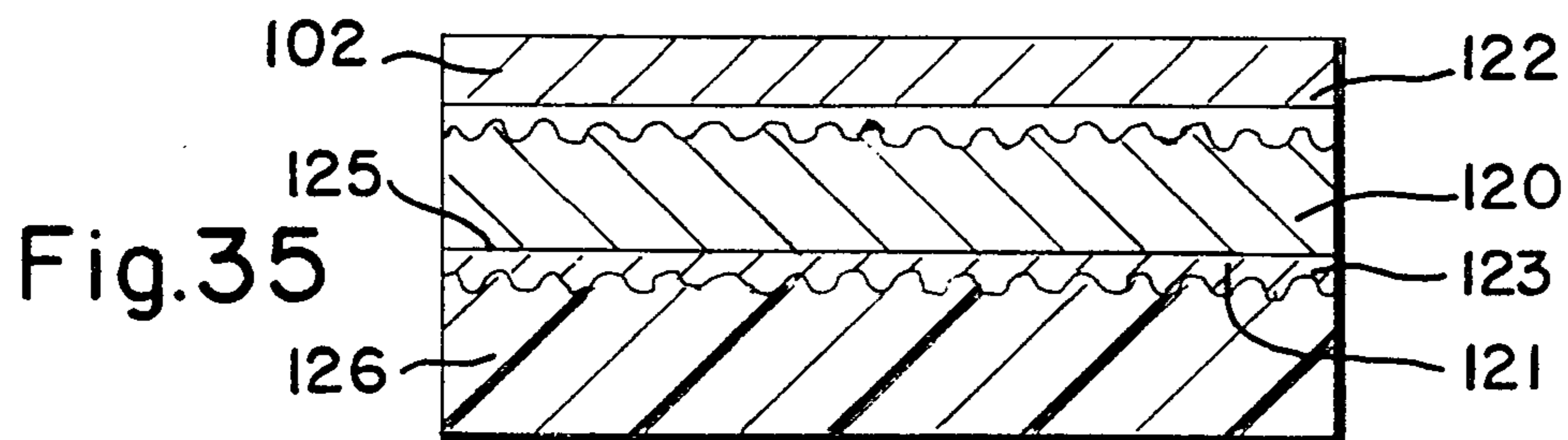
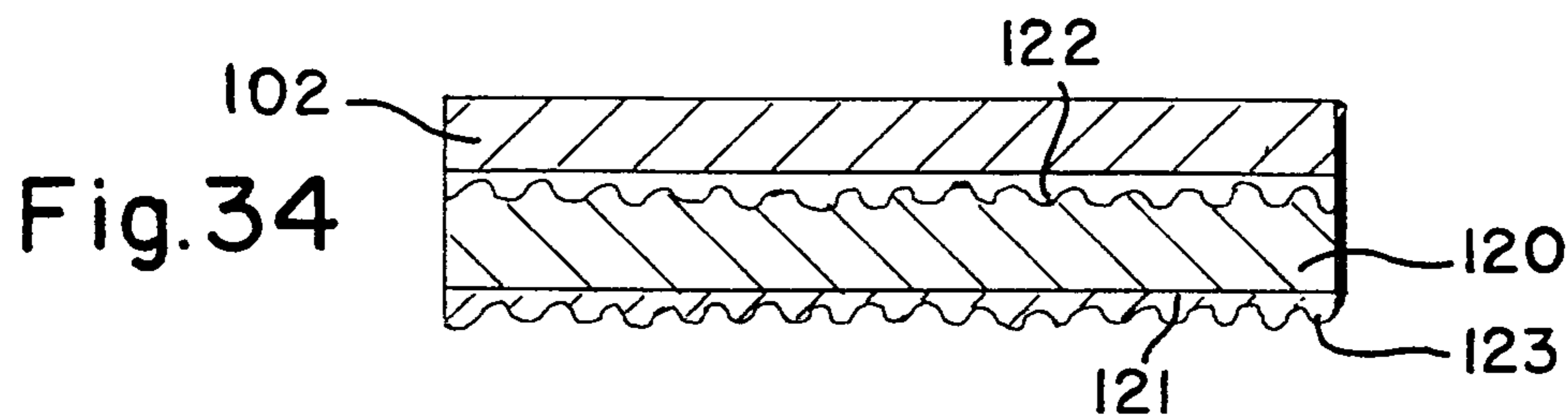
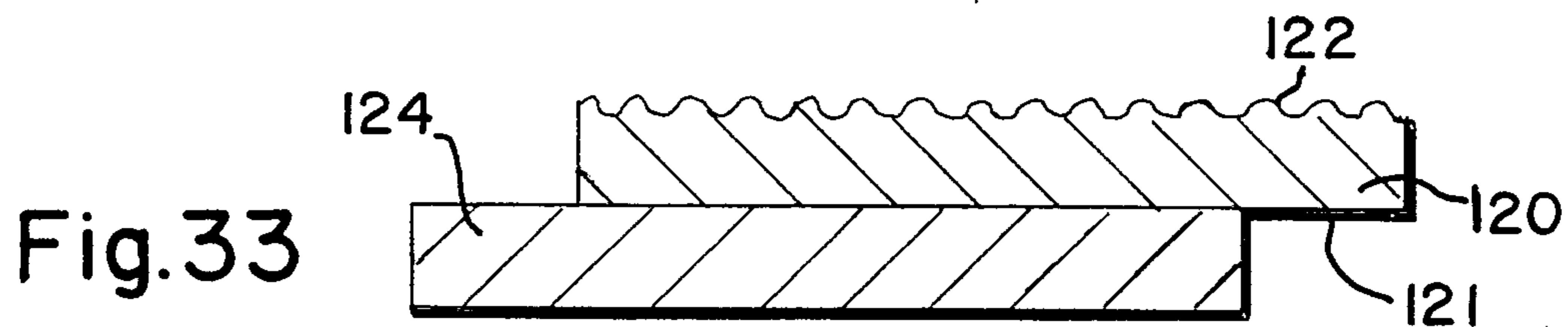


Fig.39

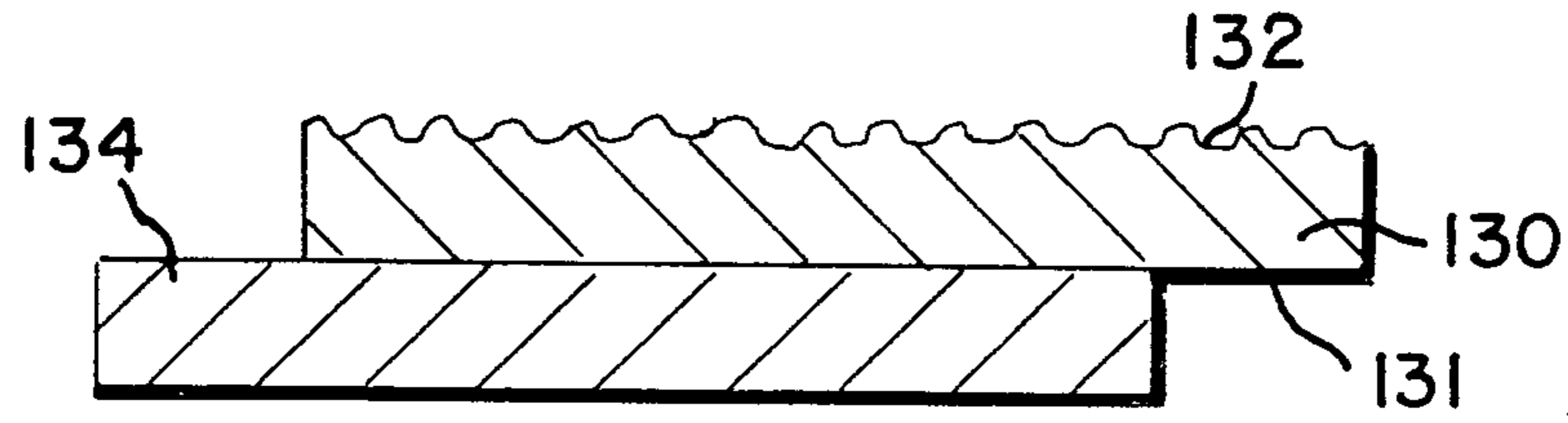


Fig.40

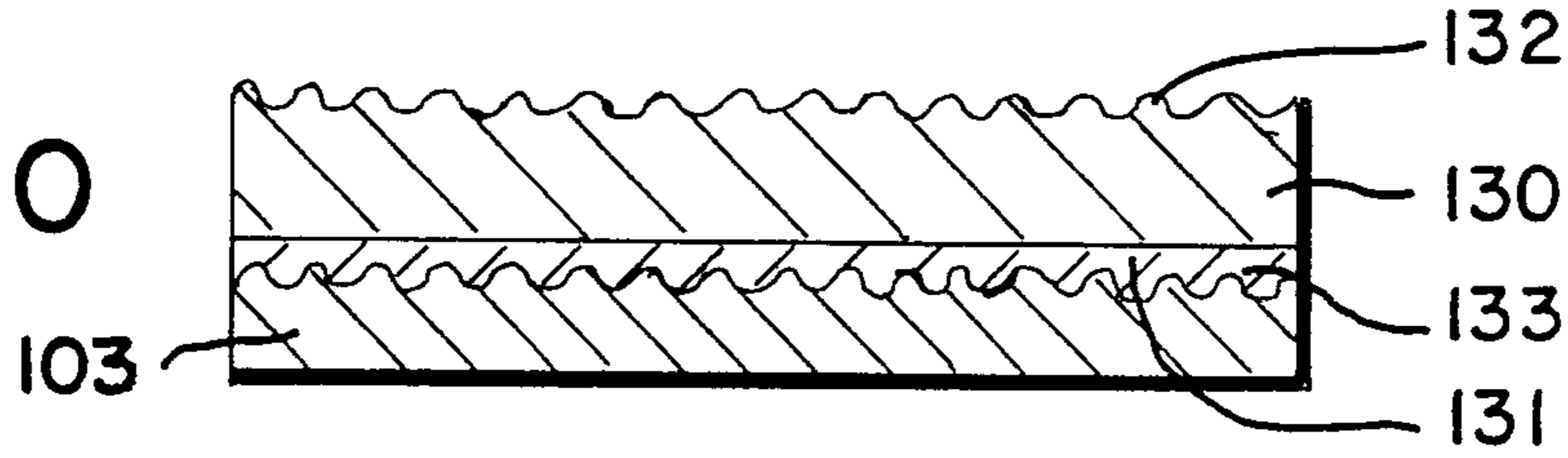


Fig.41

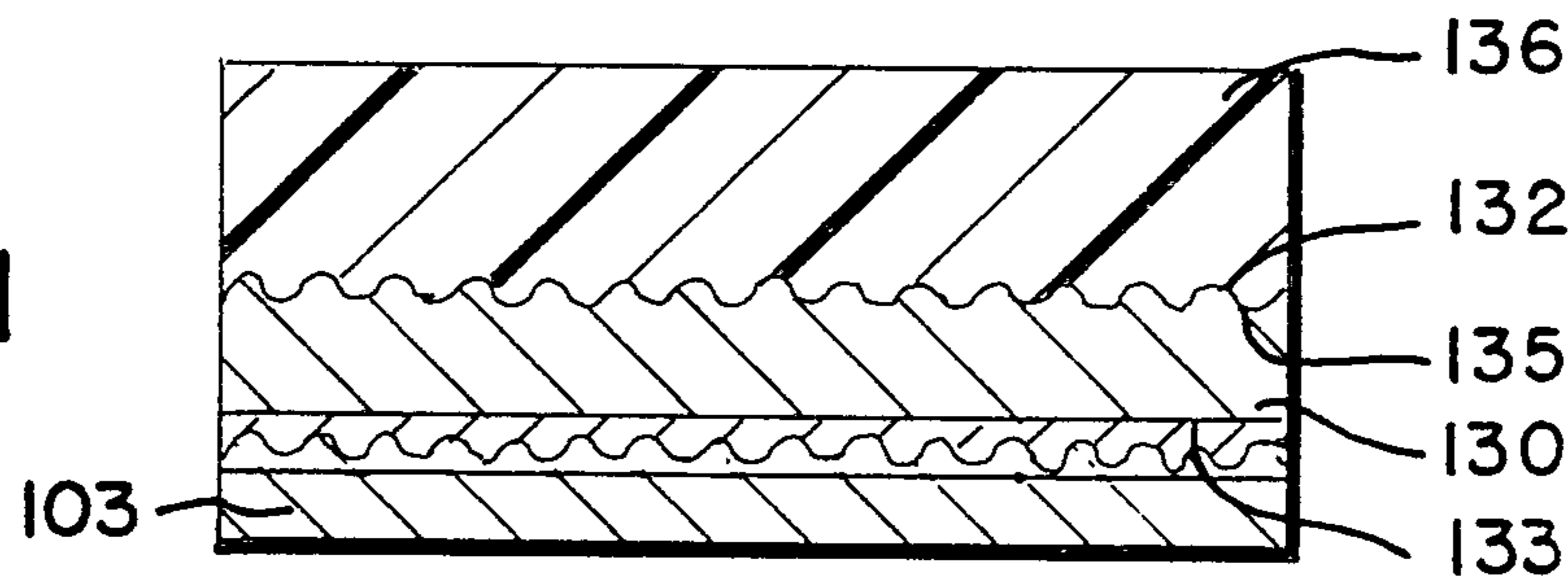


Fig.42

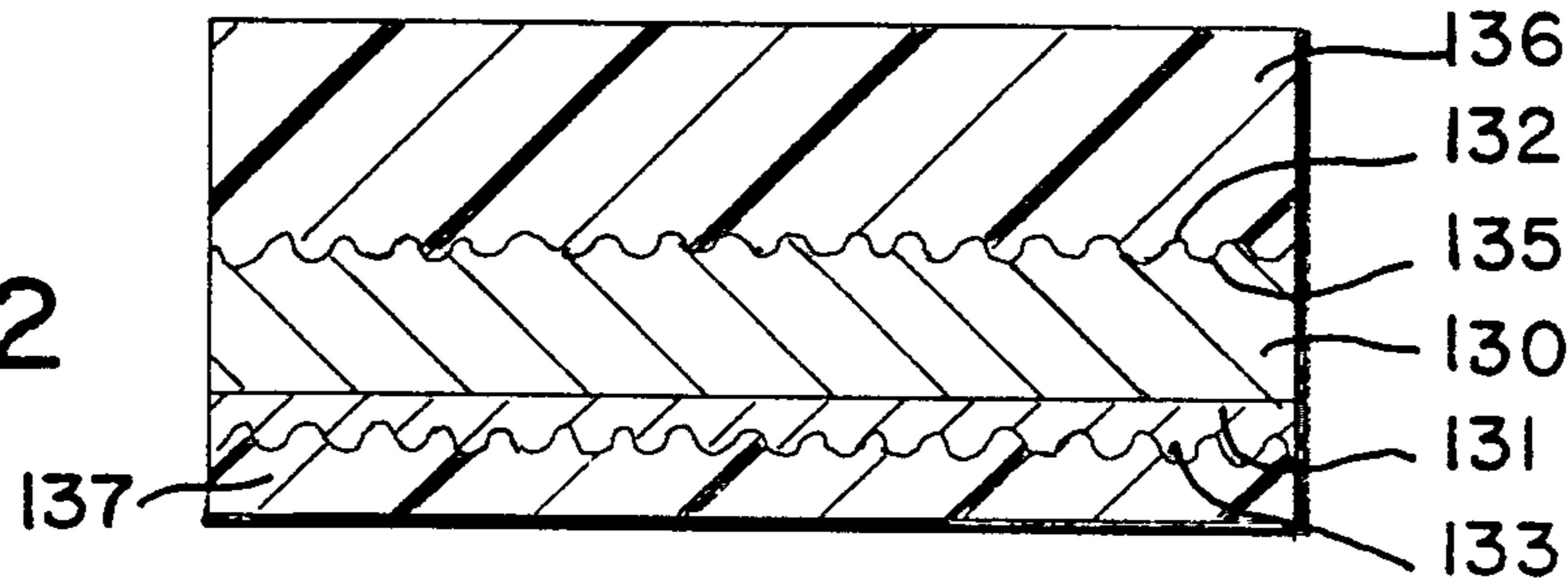


Fig.43

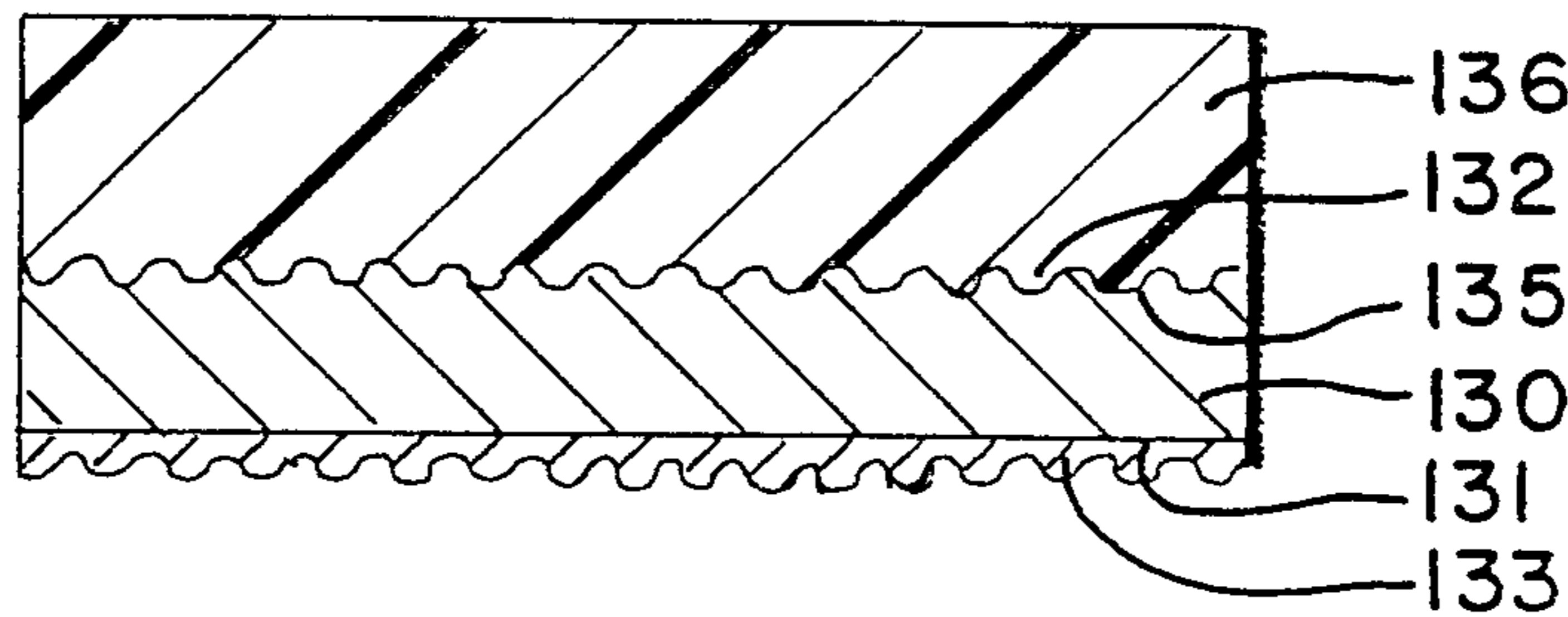


Fig.44

