

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 868 951 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.10.1998 Bulletin 1998/41

(51) Int. Cl.⁶: **B21D 51/26**, B65D 1/00

(21) Application number: **98302604.8**

(22) Date of filing: **02.04.1998**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **04.04.1997 GB 9706873**

(71) Applicants:
• **BRITISH STEEL PLC**
London NW1 5JD (GB)
• **Redicon Corporation**
Canton, Ohio 44708-1467 (US)

(72) Inventors:
• **Williams, John Selwyn**
Swansea SA4 4GE (GB)
• **Bastable, Brian John**
Swansea SA3 3JR (GB)
• **Bulso, Joseph**
Canton, Ohio 44708-1467 (US)

(74) Representative:
Fry, Alan Valentine et al
FRY HEATH & SPENCE
The Old College
53 High Street
Horley Surrey RH6 7BN (GB)

(54) **A method of producing metal cans and metal cans produced thereby**

(57) A process for producing metal cans (7) from a feedstock (1) comprising a low carbon steel strip or sheet coated on each of its surfaces with a coherent laminated coating of a thermoplastic polymer material. The process includes one or more redrawing stages in which the side walls are reduced in thickness by a stretching operation, and forming in the can base an inwardly projecting dome bordered by upstanding walls which subtend an angle of between 0 and 5° to the vertical.

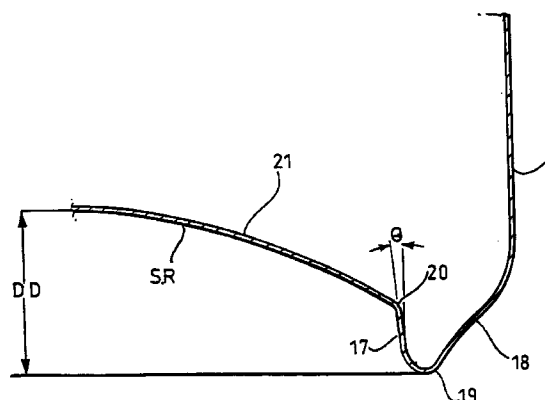


Fig.5.

EP 0 868 951 A2

Description

This invention relates to a method of producing metal cans and to metal cans produced by this method.

Metal cans such as beverage cans are conventionally produced from two pieces by a process in which the base and wall of the can is formed from a single blank of starting material. One such process is known as the drawn and wall ironed (DWI) process. In this process the starting material is tinplate or aluminum and the blank is cut and drawn into a cup which is then formed into a can shell by precise thinning of the wall. This thinning is accomplished by forcing the cup through a series of annular rings using a punch, the gap between each ring and the punch gradually decreasing thereby "ironing" the metal. The can is then cleaned and coated internally and externally with organic lacquers to provide protection against corrosion and decoration to the external can surfaces. The DWI process suffers from two major drawbacks. Firstly, the required equipment is expensive and is normally only justified when large numbers of cans are to be produced. Secondly, the process is environmentally unfriendly because large volumes of water are used to cool and clean the can and solvents and other organics are emitted during the lacquer coating process.

An alternative process is one known as the draw-redraw (DRD) process. In this process the original cup is redrawn in sequential stages to produce a can of the correct diameter and height. The starting material is conventionally electro-chromium coated steel (ECCS) pre-coated with a lacquer. This DRD process has advantages in terms of simplicity, environmental friendliness and lower capital outlay. However, more metal is used for each can produced and the pre-coated lacquer cannot be relied upon to offer sufficient corrosion protection once the can has been formed.

The present invention sets out to alleviate many of the problems associated with conventional can production processes, some of these being discussed above. In particular, the invention addresses the difficulties associated with can shaping, especially can doming. The dome of a can has to withstand high internal pressures to meet industrial standards at steels of low thickness (typically 0.15-0.16mm). Conventionally, DWI cans are internally coated with a spray coat of 'lacquer' which must cover all the exposed metal. This is difficult to achieve on surfaces close to the vertical and on sharp radii. A DWI can dome may be 'reformed' after spraying to alter geometry. Therefore, it is an object of the present invention to achieve the desired geometries without the need for reforming.

According to the present invention in one aspect, there is provided a process for producing metal cans from a feedstock comprising a low carbon steel strip or sheet coated on each of its surfaces with a coherent laminated coating of a thermoplastic polymer material, the process including one or more redrawing stages in

which the side walls are reduced in thickness by a stretching operation, and forming in the can base an inwardly projecting dome bordered by upstanding walls which subtend an angle of between 0 and 5° to the vertical.

The feedstock preferably comprises a low carbon steel strip or sheet of less than 0.25mm thickness and coated on each of its surfaces with coherent laminated films of a thermoplastic polymer, the laminate coating having sufficient formability to withstand without loss of integrity reductions in thickness of up to 40%.

The polymer laminates may comprise films of polyethylene terephthalate and polypropylene. Other film materials may however be used. The films may be bonded to the surfaces of the feedstock using heat and pressure. The films may be coextruded whereby a bonding film of approximately 2µm first makes contact with the feedstock followed by a polymer film coating which, after coating, is heated and cooled to produce an amorphous structure in the polyethylene terephthalate and a minimal crystalline structure in the polypropylene.

Preferably, the process comprises an initial cupping operation followed by first and second stretch redraw operations. Additional redraw stages may be introduced. The base of the can may be shaped to include an inwardly projecting dome during or immediately following the second stretch (or final) redraw operation. Stretching is preferably achieved by restricting - but not preventing - movement of the cupped feedstock between opposed faces of a pressure sleeve and die. One surface of the die on which the cupped feedstock seats may be recessed and a curved annular projection may extend inwardly from an upper face of the die to define a stretch point for the cupped feedstock.

Preferably, the process provides a metal can whose wall thickness is of the order of 5 to 40% less than the thickness of its base.

In a further aspect, the invention provides a metal can of low carbon steel coated with on its internal and external surfaces with a laminated coating of a thermoplastic polymer having good formability, the base of the can being formed with a dome shaped projection whose inner wall subjects an angle no greater than 5° to the vertical.

In a preferred embodiment, the feedstock for cans to be produced in accordance with this invention is double reduced high-strength high ductility low carbon steel having a proof strength in the range 480 to 690 N/mm². The maximum carbon level for the steel is typically 0.05% by weight. A typical specification for this steel is by weight %, C 0.01 - 0.04; S 0.02 max; P 0.015 max; Mn 0.15-0.30; Ni 0.04 max; Cu 0.06 max; Sn 0.02 max; As 0.01 max; Mo 0.01 max; Cr 0.06 max; Al 0.02-0.09 and N₂ 0.003 max. The steel is reduced by hot or cold rolling to a gauge typically of between 0.12mm and 0.25mm and is processed by known appropriate heating cycles and continuous annealing. The steel has a minimum earing quality and a strength typically in the

range 500 to 600N/mm².

Typically, the steel is a high strength ductile steel known as TENFORM DR (RTM).

Strip produced from the feedstock may then be subjected to an electrolytic coating process. In this process, the steel strip is cleaned and pickled before being passed through a plating bath in which it is coated with a thin layer of chromium metal (typically of 0.01µm thickness) followed by a thin layer of chromium oxide (again typically of 0.01µm thickness). Alternatively, tinplate, blackplate or other suitable substrate could be employed.

The strip is then laminated with a polymer material, typically that known under the name "Ferrolite" (RTM). In this laminating process a film of PET (polyethylene terephthalate) and/or PP (polypropylene) and/or nylon either separately or simultaneously is bonded to the surface of the metallic coated steel strip or sheet using heat and pressure. The films are co-extruded so that a bonding layer of ~ 2µm first makes contact with the steel and forms a strong bond. After the bond is formed with the substrate the polymer films are melted and held above the recrystallisation temperatures for a few seconds before being rapidly quenched to below their softening temperatures. This produces an amorphous structure in the PET and a minimal crystalline structure in the PP.

No solvent emissions result from this laminating process.

Typically the thickness of the external polymer coating is of the order of 25µm thickness and the internal thickness is between 15 and 30µm.

Laminating processes and polymer films of a different structure and composition other than those discussed may be employed.

The strip, either in sheet or coil form, is fed to a cupper either in a pre waxed condition or is passed through a waxer on entry to the cupping system. The wax may be edible and petroleum based with film weights in the range of 5-20 mg/ft². At this stage the laminate may be heated in the range 70°-120°C. Alternatively the heating process may be carried out after the cupping or first redrawing stage. Pre-heating relieves stresses and ageing effects in the laminate so that subsequent forming is carried out more easily. Discs are stamped from the strip or sheet. The cup is stretch drawn in one operation using a disc with a diameter typically in the range 150mm to 200mm. This diameter is dependent (with gauge) upon the required can size and type of application. The draw ratio (i.e. ratio of the diameter of the disc to that of the cup) is typically in the range 1.0-2.0:1. The geometry of the tooling is designed in combination with the correct blank holding load to give a reduction in wall thickness at the cupping stage of up to 10%. This is accomplished with a die radius range typically between 0.5mm and 1.5mm and a parallel land length of up to 5mm. The blank holding load is achieved by use of a boosted air pressure of up to 200 psi fed into a series (typically three) of internal multiplying pistons. The

punch/die gap is important and is controlled by the feedstock gauge and coating and gaps of 1.20 - 1.50 times the starting total laminate thickness are typically used. The punch nose radius is carefully controlled to achieve the required stretch whilst minimising subsequent can wall marking which could lead to laminate rupture. Punch nose radii in the range 2.5mm to 7mm are generally required.

The copper cup is passed into the stretch redraw press which contains tooling for both first and second redraw operations. The diameter of the cup is reduced in the first redraw operation with a draw ratio in the range 1.0-1.7:1, and with a wall thickness reduction of up to 25% of the ingoing cup wall thickness. The wall thickness reduction is achieved by a stretching technique. The wall thickness reduction is balanced with the draw ratio and is achieved by use of pressure sleeve and die geometries in combination with controlled blank holding loads. The tooling geometries typically fall in the following ranges:

- pressure sleeve diameter up to 0.66mm smaller than the copper cup ID;
- pressure sleeve radius up to 2.0mm;
- die radius up to 2mm with a parallel land length up to 5mm.

The blankholding load is achieved by use of air pressure of up to 100 psi fed into a stack of two or more internal multiplying pistons.

Location of the cup on the die is effected by means of a nest recess with a diameter matched to the copper cup, allowing for the thickness of the actual laminate in use. The radius of the nest diameter with the die at the base of the nest is in the range 0.10 - 2.00mm.

The punch has a taper which is typically between 40mm and 60mm from the punch nose with an increase in punch diameter of 0.25mm to 0.50mm to aid stripping. The gap between the largest punch diameter and die (per side) is generally controlled to between 1.20 and 1.50 times the starting laminate thickness. The punch radius is important to achieve the required stretch whilst minimising subsequent can wall marking which could lead to laminate rupture. Punch nose radii in the range 1mm to 3mm are typically used.

Gap control or arrested draw is employed at the first redraw stage to diameter matched to the first redraw cup, allowing for the thickness of the actual laminate in use. The radius of the nest diameter with the die at the base of the nest is typically in the range 0.10 - 2.0mm.

The punch has a taper located between 15mm and 30mm from the top of the second redraw cup in the range 0.10mm - 0.25mm increase in diameter to aid stripping of the can from the punch. The gap between the punch and the die (per side) at the widest point is controlled to between 1.0 and 1.20 times the starting laminate thickness.

Gap control or arrested draw is employed again as

the second redraw stage to eliminate cup high spot clip offs or the generation of laminate "whiskers". When gap control is used, gaps of 0.10mm to 0.15mm are used between the pressure sleeve and die face dependent upon the laminate feedstock used. The overall can wall thinning employed is 5 - 40% dependent upon the end use of the can.

A dome is formed in the can at this stage by use of a doming station with a forming ring acting as a blank holder. The blankholding load on the form ring is achieved by use of a boosted air pressure up to 500 psi fed into a series (typically three) of internal stacked pistons. The positions of the forming ring relative to the dome die is important in that the ring must clamp the laminate to the dome chime of the punch before the dome die starts to draw the dome. For carbonated beverage cans, domes of 202, 204 and 206 are used.

The dome profile must be capable of withstanding a dome reversal pressure of 90 - 100 psi depending upon can contents (pasteurised or non pasteurised). The dome, the can walls and neck must be capable of withstanding an axial load of 1.0KN. This is achieved by the combination of the high strength formable DR steel and the geometry of the design. It is also facilitated by the polymer laminate coatings which can withstand the eliminate cup high spot clip offs or the generation of laminate "Whiskers". When gap control is used, gaps of 0.10 to 0.15mm between the pressure sleeve and die face are generally used depending upon the laminate feedstock used.

A small reverse draw in the cup base may also be used in this operation depending upon the dome required in the final can. Domes for carbonated beverages may be 206 (2 6/16 inches), 204 or 202 diameter. The purpose of the reverse draw is to eliminate the tendency to form chime wrinkles in the finished can and to make the cup base more rigid and thus keep the can circular and eliminate the tendency for oval cans.

The first redraw cup is passed back into the stretch redraw press in a station containing the second redraw tooling. The cup diameter is reduced in this operation to the final can diameter. This may be 211 for normal beverage cans or 209 for shaped beverage cans. The draw ratio used is generally in the range 1.0-1.7:1 with a wall thickness reduction of up to 25% of the ingoing cup wall thickness. The wall thickness reduction is again achieved by a stretching technique using a combination of pressure sleeve and die geometries with controlled blankholding loads. The correct choice of diameter reduction ratio to achieve the finished can is also important in enabling the stretching process to be successful. The tooling geometries used are typically in the following ranges:

- pressure sleeve diameter up to 0.30mm smaller than the first redraw cup internal diameter;
- pressure sleeve radius up to 2.0mm;
- die radius up to 2mm with a parallel land length up

to 5mm.

The blankholding load is achieved by use of air pressure up to 100 psi fed into a stack of two or more internal multiplying pistons.

Location of the cup on the die is by means of a nest recess with a forming operations and still offer protection at sharp radii and angles. Normally DWI cans are internally coated with a spray coat of 'lacquer' which must cover all exposed metal, but this is difficult to achieve on surfaces close to the vertical and on sharp radii. A DWI can dome may be 'reformed' after spraying to alter geometry but in this can the geometry described below is achieved without reforming.

The necessary features are the depth of the dome, which is preferably > 11mm, the spherical radius of the dome, which preferably lies between 48 and 54mm, the radius at the the point where the inner upstanding wall meets the spherical dome is preferably less than 0.6mm and most importantly, the angle made between the upstanding walls (which border the inwardly projecting dome) should lie between 0 and 5° to the vertical.

After the final redraw the can is trimmed and passed through an oven. This oven is typically held at 200-230°C and the pass time is typically between 1 and 3 minutes. This facilitates the removal of petroleum wax lubricant to such a level so that it does not interfere with the laydown of printing inks used to decorate the can. It also raises the surface energy of the PET coating to at least 38 dynes/cm which increases the wettability of the PET surface to printing inks. The temperature cycle in the oven is chosen to minimise recrystallisation of the PET by rapid temperature rise and cooling times.

Printing is currently carried out using conventional machinery which applies thermally curing inks onto the external surface of the can. Again, recrystallisation of the PET is minimised as above. Alternatively a shrink-wrap sleeve may be applied at lower temperatures.

Can fillers are continually seeking methods of product differentiation in various forms. To date, this has mainly been achieved by the use of various decorations and decorating techniques. Another method of product differentiation being sought is by the use of shaped cans. The shaping of three-piece cans, particularly in the speciality packaging market, has been used for many years but the shaping of two-piece cans has hitherto been unknown. The key to the solution of can shaping is the formability inherent in the can wall presented to the shaping machine. There are various methods of achieving the desired shape, but all rely on a measure of formability, given by a combination of can wall thickness and ductility. Three-piece cans have can walls with mechanical properties and thickness essentially the same as the ingoing plate. Two-piece cans have walls that are thinner than the starting material and hence due to strain hardening effects, stronger and less ductile than the starting material.

Different methods of can shaping require differing

levels of formability and hence the level of formability left in a can wall will dictate the method of shaping that is likely to prove successful.

For 211 diameter beverage cans, the maximum outside can diameter at any point on the can after shaping should remain at 211 but for some applications increased diameter would be suitable. The reason for this is that this will minimise any disruption to existing filling lines, since, with any can making development, cost is by far the biggest driver. The trend, therefore, has been to manufacture cans with a smaller diameter, typically 209 and expand to 211 in various ways. This implies a diametrical expansion requirement of ~ 5.0%. The diametrical expansion possible by simple stretch forming alone on steel DWI cans varying from light-weight through to heavyweight cans has been measured at 0.7% - 1.2%. That for cans in accordance with this invention is 1.6% and that for aluminium DWI cans is 3.6%. These results indicate that if the can is to be shaped to current expected levels, then the deformation for all cans cannot be by stretch alone. However, these results indicate varying levels of formability and whereas the aluminum DWI cans claims of successful shaping have been made, increases of up to 30% of wall thickness are needed to achieve this. After shaping, the can still has to comply with the mechanical properties required of the can, particularly axial crush levels. Since aluminium cans do not exhibit strain hardening properties then the axial crush strength of a shaped aluminium can is very low.

Whilst steel DWI cans have been successfully shaped, the process route involves intermediate treatment and/or advanced forming techniques which add significantly to be manufacturing cost.

Cans in accordance with the invention however, have been shaped successfully and with diametrical expansions recorded of 10% with much higher levels expected. This is possible with the increased formability of the can wall resulting from the special steel and production route used which is designed to increase ductility with little reduction in strength. This property, coupled with the strain hardening property of the steel also results in the formation of a shaped can with relatively high axial crush strength. Shaping is typically achieved using expandable mandrels which locate within the can interior, but other methods (such as hydro-forming) are possible.

A further advantage of the present invention is that if either an aluminium or steel DWI can is shaped, coating is particularly difficult with the problems of internal lacquer damage and the difficulty of internally spraying a shaped can. Cans in accordance with the invention are particularly suited since the coating is abrasion resistance and withstands current shaping operations, whilst maintaining good corrosion protection.

Also, no internal lacquers or external base coats are required.

The invention will now be further described by way

of example only with reference to the accompanying diagrammatic drawings, in which:-

Figure 1 illustrates five stages of a cupping operation of the method of the present invention;

Figure 2 illustrates five stages of a first stretch redraw operation of the method of the present invention;

Figure 3 illustrates six stages of a second stretch redraw operation of the method of the present invention;

Figure 4 is a detail to an enlarged scale of a stretch redraw operation in accordance with the invention; and

Figure 5 is a half-section taken through a can produced in accordance with the invention.

Figure 1 shows five stages of a cupping operation of the method of the present invention. The five stages are labeled A to E. Stage 1A shows a feedstock strip 1 of laminated steel strip held between a draw pad 2 and a blank and draw die 3. A disc 4 of the required diameter is cut from the strip, by downward movement of a cutter 5 (see Figure 1B). A punch 6 (Figures 1C and 1D) is then moved downwardly with the disc edges trapped between the opposed surfaces of the draw pad 2 and draw die 3. A cup 7 is thereby formed which is removed from the die by air pressure (see Figure 1E).

Typically, the feedstock strip is of the order of 0.16mm gauge. This compares with a gauge of around 0.28mm for conventional aluminum feedstock.

As will be seen from Figure 2, the cup 7 is then placed on a die 8 for first redraw purposes. This stage is illustrated in Figure 2A. The die is formed with a shaped lip 9 and has a curved annular projection 10 protruding inwardly from its upper surface. The lip 9 and projection 10 can be seen more clearly from Figure 4. As seen in Figure 2B, a pressure sleeve 11 and punch 12 move downwardly and within the side wall of the cup 7. The outer rim of the cup base seats between the opposed surfaces of the pressure sleeve 11 and the die 8. The gap between these members is sufficient only to restrict movement of the cup 7, not to impose a force sufficient to deform or iron the cup. As the punch is moved downwardly, so the cup wall is stretched to increase cup height. This stretching process can be seen more clearly from Figure 4. It will be seen that the cup wall between the projection 10 and the punch lower face is not in contact with either the die 8 or the side wall of the punch 12. Movement of the cup between the pressure sleeve 11 and the die 8 and over the curvilinear projection 10 is restricted to cause stretching of the cup wall.

After stretching, the cup is ejected by air pressure (see Figure 2E).

Turning now to Figure 3, the second redraw operation uses the same or very similar pressure sleeve and die as those used in the first redraw operation. These have accordingly been given the same reference numerals.

In Figure 3, the cup 7 is again shown positioned on the die 8. See Figure 3A. The pressure sleeve 11 is moved downwardly as shown in Figure 3B to position the sleeve within the cup 7. Again, the spacing between the sleeve 11 and the die 8 is to restrict movement of the cup, not to preclude such movement.

A punch 14 including a recessed base 15 is moved downwardly into engagement with the cup base to once again stretch the cup side wall and effect elongation thereof. The stretching operation being as described above in relation to Figure 2. This stretching operation is shown in Figures 3C and 3D. After the cup leaves the die 8 continual downward movement of the punch 14 places the cup base into engagement with a dome die 16 and a forming ring 17 which operate to produce in the cup base a required dome which imparts strength to the finished article.

The fully stretched and formed cup is the ejected using air pressure as shown in Figure 3F.

Typically, the fully stretched and formed cup has a midwall thickness of around 0.12mm and a top wall thickness of around 0.15mm. These dimensions compare with 0.104mm and 0.165mm respectively for conventional aluminium cans.

The shape imposed in the can base by the forming ring and dome die is shown in Figure 5. This dome has to withstand internal pressures of at least 95 psi to meet current industrial standards at steel thicknesses below 0.20mm (typically 0.15/0.16mm). This is achieved by the combination of the high strength formable DR steel and the geometry of the design. It is also facilitated by the polymer laminate coatings which can withstand the forming operations and still offer protection at sharp radii and angles. Normally DWI cans are internally coated with a spray coat of 'lacquer' which must cover all exposed metal, but this is difficult to achieve on surfaces close to the vertical and on sharp radii. A DWI can dome may be 'reformed' after spraying to alter geometry but in this can the geometry described below is achieved without reforming. With reference to Figure 5, the important features are the depth of the dome, DD, which should be > 11mm, the spherical radius of the dome, SR, which should lie between 48 and 54mm, the radius at position 20 which should be less than 0.6mm and the angle θ which should lie between 0 and 5°.

If the can is to be shaped, this can be achieved by insertion of an expandable mandrel which, once expanded, imposes any required shape to the can. This is possible only because of the particular pre-coated laminated strip feedstock employed which has sufficient inherent formability to withstand the stretching and forming operation discussed without any loss of coating integrity. Other can shaping processes including hydro-

forming can be employed.

It will be apparent from the foregoing that the invention provides can shaping by mechanical expansion (typically up to 10%) with no intermediate treatment, upgauging or lacquer repair system required. Thus, the expansion potential for lightweight cans is maximised and the higher strength and work hardening achieved results in improved axial crush performance. Also, solvent emissions are virtually eliminated and all coatings are PVC free. Waste products from the can making process are also significantly reduced.

It will be appreciated that the foregoing is merely exemplary of methods and apparatus in accordance with this invention and that modifications can readily be made thereto without departing from the true scope of the invention.

Claims

1. A process for producing metal cans from a feedstock comprising a low carbon steel strip or sheet coated on each of its surfaces with a coherent laminated coating of a thermoplastic polymer material, the process including one or more redrawing stages in which the side walls are reduced in thickness by a stretching operation, and forming in the can base an inwardly projecting dome bordered by upstanding walls which subtend an angle of between 0 and 5° to the vertical.
2. A metal can of low carbon steel coated with on its internal and external surfaces with a laminated coating of a thermoplastic polymer having good formability, the base of the can being formed with a dome shaped projection whose inner wall subjects an angle no greater than 5° to the vertical.
3. A metal can as claimed in claim 2 of double reduced high-strength high ductility low carbon steel having a proof strength in the range 480 to 690 N/mm².
4. A metal can as claimed in claim 3 wherein the maximum carbon level for the steel is 0.05% by weight.
5. A metal can as claimed in claim 4 including by weight %, C 0.01-0.04; S 0.02 max; P 0.015 max; Mn 0.15-0.30; Ni 0.04 max; Cu 0.06 max; Sn 0.02 max; As 0.01 max; Mo 0.01 max; Cr 0.06 max; Al 0.02-0.09 and N₂ 0.003 max.
6. A metal can as claimed in any one of claims 2 to 5 wherein the steel is reduced by hot or cold rolling to a gauge of between 0.12mm and 0.25mm.
7. A metal can as herein described and as herein described with reference to the accompanying diagrammatic drawings.

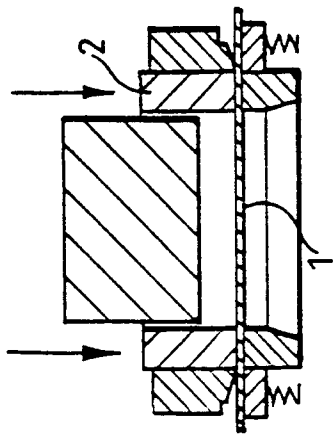


Fig.1A.

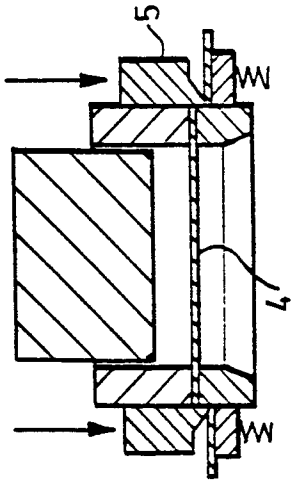


Fig.1B.

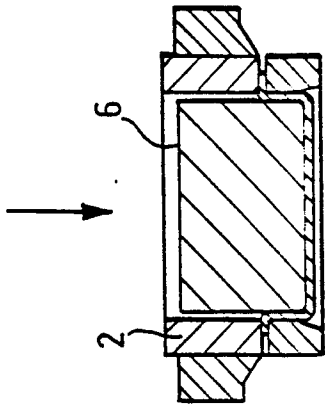


Fig.1C

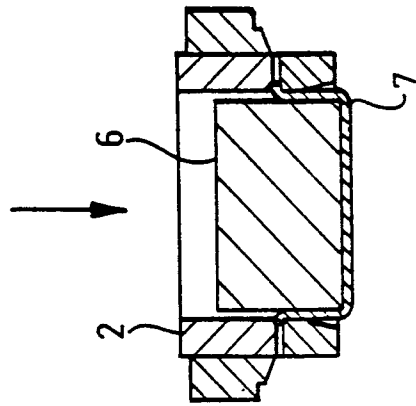


Fig.1D.

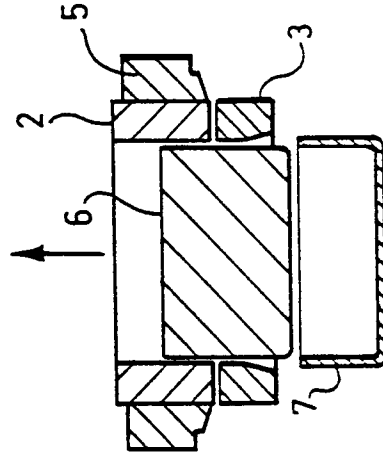


Fig.1E.

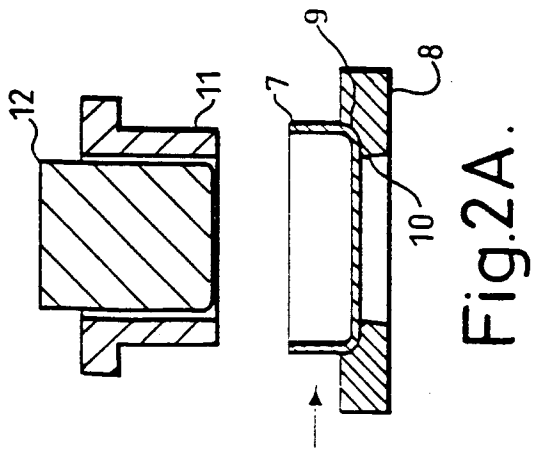


Fig. 2A.

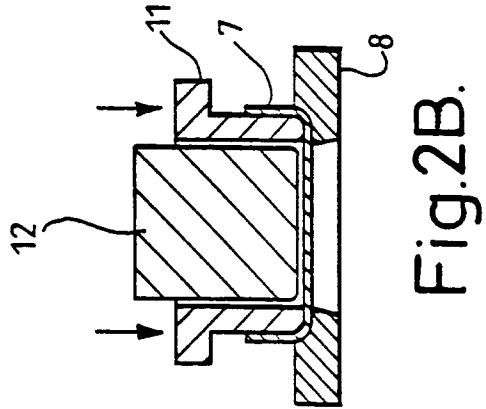


Fig. 2B.

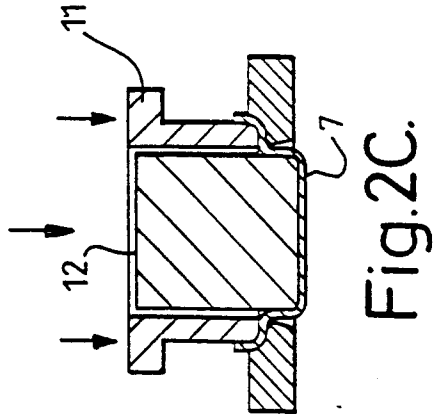


Fig. 2C.

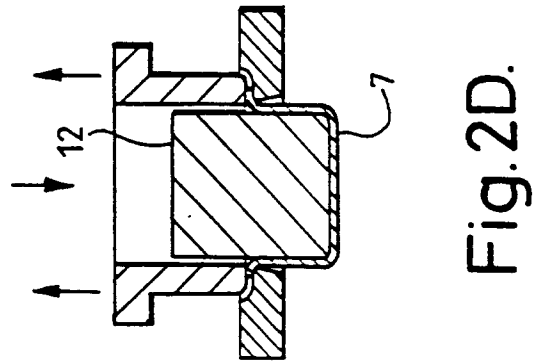


Fig. 2D.

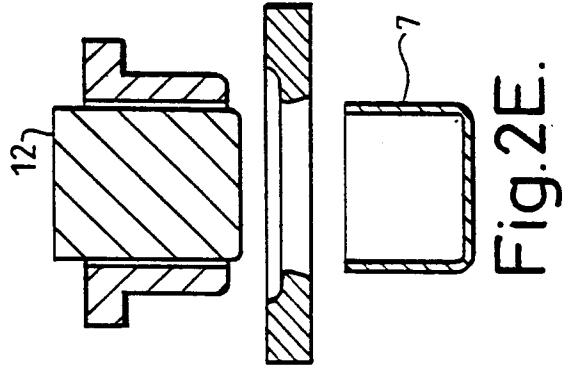


Fig. 2E.

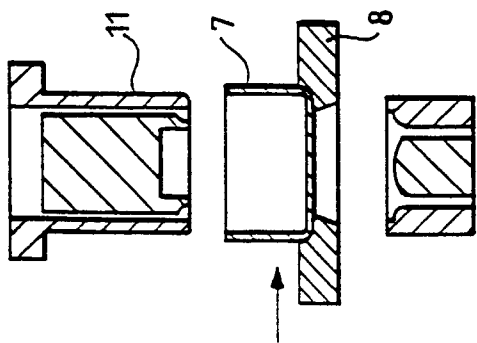


Fig.3A.

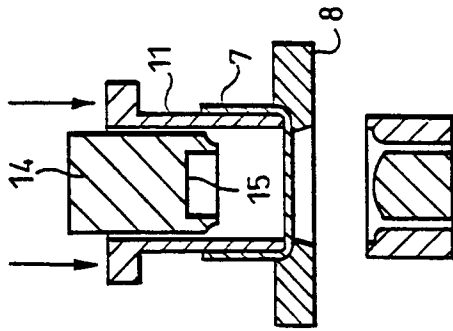


Fig.3B.

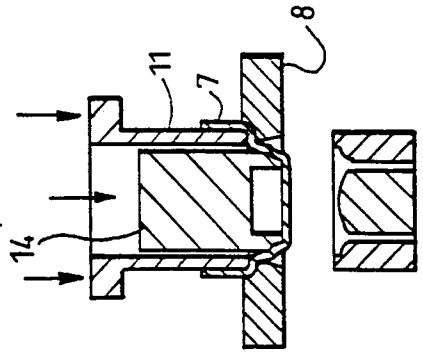


Fig.3C.

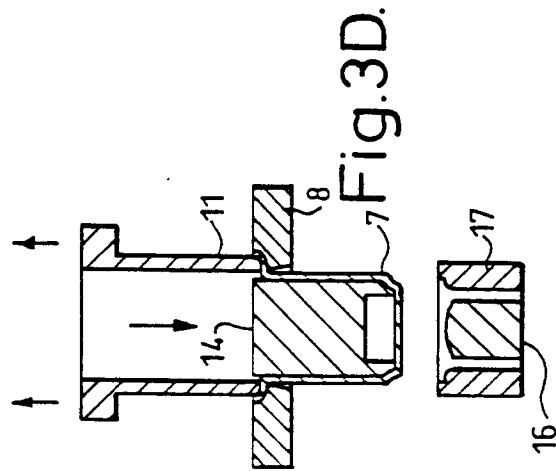


Fig.3D.

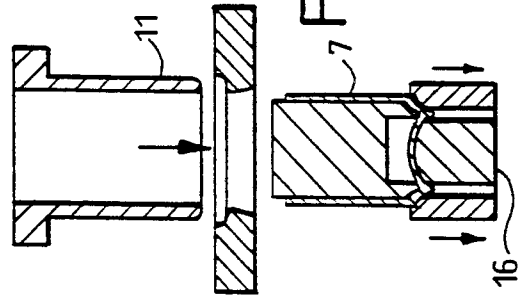


Fig.3E.

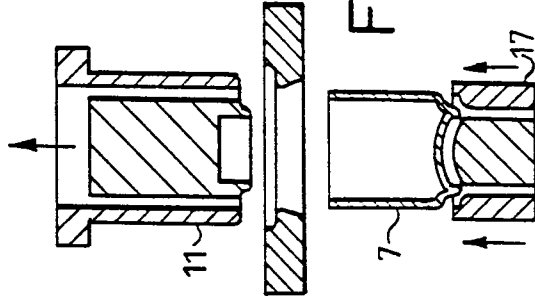


Fig.3F.

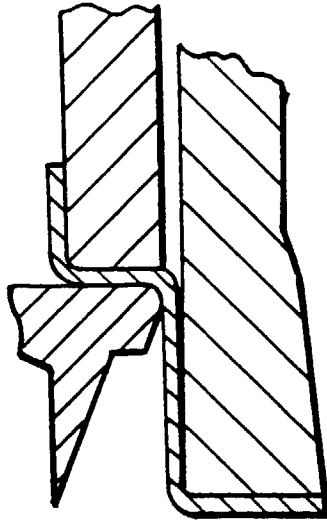


Fig.4.

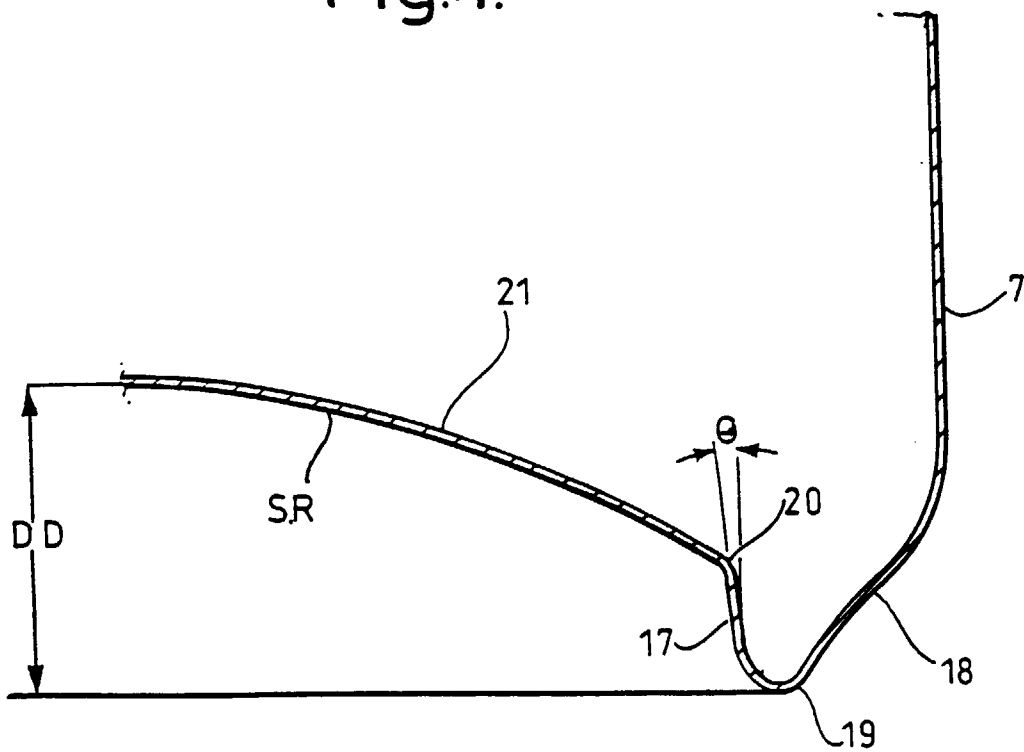


Fig.5.