

[54] **MOLECULARLY ORIENTED BOTTLE**

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3,757,978 9/1973 Gilbert 215/1 C

FOREIGN PATENTS OR APPLICATIONS

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[57]

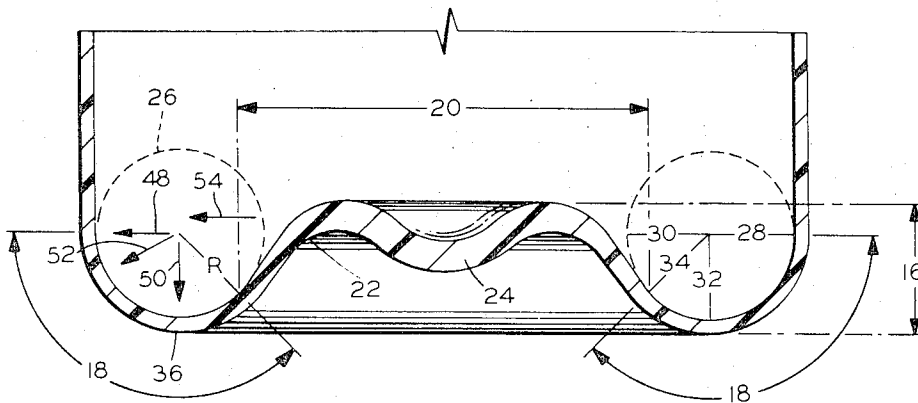
ABSTRACT

A bottle for carbonated soft drinks and beer having enhanced resistance to impact and burst pressure which is formed from a polymer wherein the major constituent is polymerized acrylonitrile monomer. The bottle has a bottom portion comprising a substantially toroidal segment merging at one end into the lower end of the sidewall and at its other end into an inner base wall closing off the bottom of the bottle, the radius of curvature of said toroidal segment being between 10 to 20 percent of the maximum diameter of the generally cylindrical body and the surface area of said segment being at least 30 percent of that of a full torus. The polymer of the substantially toroidal segment is molecularly oriented exhibiting an orientation release stress of at least 50 psi in both the axial and circumferential directions.

11 Claims, 2 Drawing Figures

[56] **References Cited**
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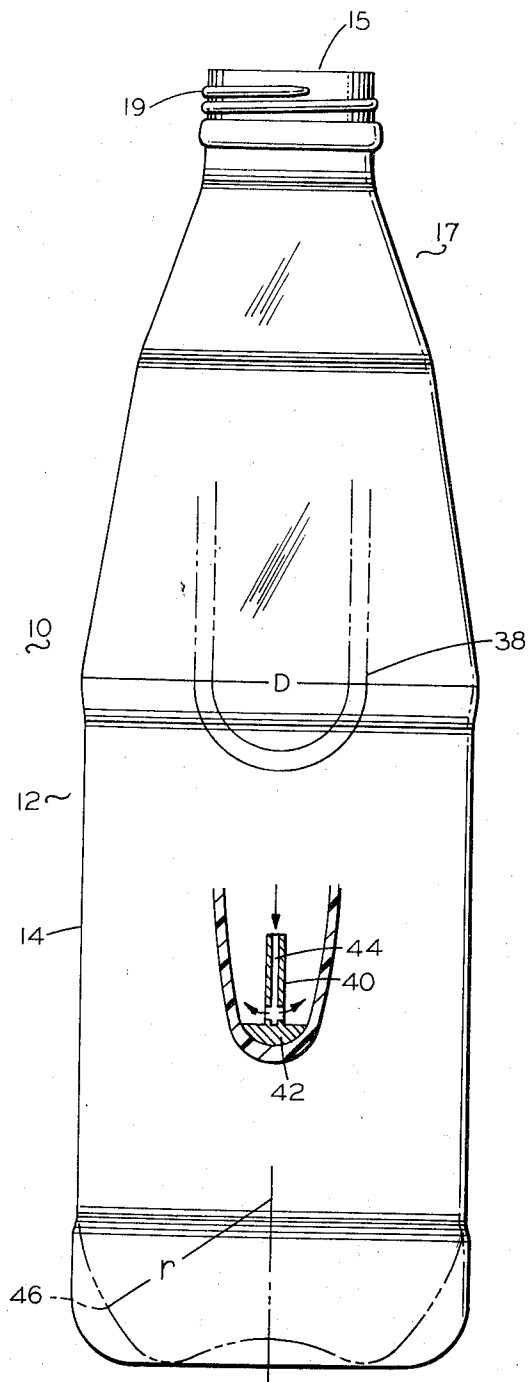


FIG. 1

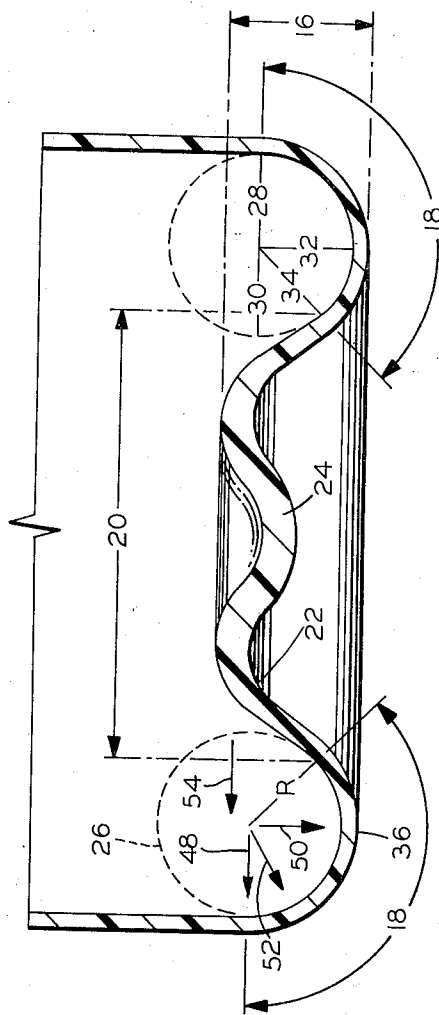


FIG. 2

MOLECULARLY ORIENTED BOTTLE

BACKGROUND OF THE INVENTION

This invention is directed toward tough, high strength bottles for packaging beverages such as carbonated soft drinks and beer.

It has recently become known to package beverages such as carbonated soft drinks and beer in disposable plastic containers. To be a successful packaging media in such applications the thermoplastic material chosen must have gas and liquid barrier properties which are adequate to preserve the integrity of the contents over normal shelf life periods of the package. For example, carbon dioxide and water loss from the contents or oxygen gain through the wall of the container must be kept below certain maximum levels. In addition, the container must be able to withstand the rather substantial internal pressures generated by the contents without disintegrating, such pressures ranging as high as 200 psig under severe storage temperature conditions. Nitrile-based polymers have been recognized in the art as having the properties necessary to qualify for such pressurized packaging applications.

In copending, commonly assigned, U.S. application Ser. No. 75,094, filed Sept. 24, 1970, now U.S. Pat. No. 3,720,339, there is disclosed a particular form of bottle base configuration which minimizes stress buildup in the lower wall portion of the container due to the internal pressure of the contents and distributes same such that the stress developed never exceeds the tensile strength of the polymer from which it is formed. Such a design utilizes generous radii in the transition area between the sidewall and base where the stress levels are known to be highest, as do other prior art, one piece container configurations for use with beverages under pressure such as those described in U.S. Pat. Nos. 3,511,401 and 3,643,829. In all of these configurations, the radius in the chime area of the bottle or in the section between the base and sidewall is typically about $\frac{1}{2}$ to $1\frac{1}{2}$ or more times the major bottle diameter in order to achieve the intended purpose of utilizing the container design to keep the stress buildup below that which the polymer of the bottle can withstand, and such configurations serve quite well for their intended purpose.

However, when the bottle is formed from a nitrile-based polymer, other problems occur in that such polymers tend to be brittle by nature, and one of the necessary commercial requirements of a beverage container is that it have a degree of impact resistance at least sufficient to withstand falls from reasonable heights, as well as exposure to various impact blows which inevitably occur during filling and processing, without rupturing.

It has been traditional in the art to incorporate rubber into polymers to improve such impact strength, such rubber serving as an energy absorbing material. However, in addition to the increase in polymer cost occasioned by incorporating another component into it, the presence of rubber in a polymer at levels sufficient to markedly improve impact strength (5-15 percent) tend to undesirably rather substantially increase permeability.

Similarly, molecular orientation of polymers, and specifically high nitrile polymers (see, e.g., U.S. Pat. Nos. 3,458,617 and 3,615,710) for the purpose of im-

proving impact strength is known in the art as an alternative to or combinable with incorporation of an impact modifying material into the plastic.

It would thus seem as though forming a bottle of a high nitrile polymer while at molecular orientation temperature and with a low stress base configuration such as that shown in the aforementioned copending application would provide a container which is highly functional for packaging beverages under super-atmospheric pressure.

However, heretofore attempts to utilize such bottle base configurations as previously described while developing molecular orientation in the polymer in the chime area of the bottle where impact usually occurs, which is sufficient to provide the impact strength required during normal handling and use, have not been successful.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of this invention to provide an improved bottle for carbonated beverage, beer and other related packaging applications.

Another object of this invention is to provide such a bottle made of a polymer wherein the major constituent is polymerized acrylonitrile monomer.

A further object of this invention is to provide such a bottle formed from an acrylonitrile-based monomer having improved toughness obtained through molecular orientation techniques.

An additional object of this invention is to provide such a bottle having a lower body configuration designed to optimize the amount of orientation that can be developed in the acrylonitrile-based polymer during formation of the bottle.

Another object of this invention is to provide such a bottle having a lower body configuration which provides optimum molecular orientation in the body wall without sacrificing the stress retention capability characteristic of the container.

Yet a further object of this invention is to provide a lower body design in a bottle for a carbonated beverage formed from a nitrile-based polymer wherein strength (ability to withstand stress) is relatively balanced with toughness (ability to withstand impact shock).

Other objects of this invention will in part be obvious and will in part appear hereinafter.

These and other objects are accomplished by providing a bottle for a beverage under pressure formed of a polymer wherein the major constituent is polymerized acrylonitrile monomer, said bottle comprising a generally cylindrical body which includes a sidewall portion having a discharge opening at its upper end and means formed therein adjacent said opening for cooperating with a pressure confining closure, a bottom portion at the other end of the sidewall portion comprising a special, toroidal segment between the sidewall and an inner base wall closing off the bottom portion of the bottle, the radius of curvature of such toroidal segment being between 10 to 20 percent of the maximum diameter of the generally cylindrical body and the surface area of such toroidal segment being at least 30 percent of that of a full torus, the polymer of said segment being molecularly oriented, exhibiting an orientation release stress of at least 50 psi in both the axial and circumferential directions.

The inner base wall which closes off the lower end of the bottle preferably has a curved portion having a ra-

dus substantially equal to but reverse from the radius of curvature of the toroidal segment, such curved portion merging into the segment and having a height above the lowermost point of the segment of between 5 to 30 percent of the greatest diameter of the body of the bottle.

BRIEF DESCRIPTION OF THE DRAWING

In describing the overall invention, reference will be made to the accompanying drawing wherein:

FIG. 1 is a schematic elevational view of a bottle embodying the present invention; and

FIG. 2 is a sectional view of the lower portion of the bottle of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic material from which the bottle of the present invention is made must be a polymer wherein the major constituent (at least 55 weight percent) is polymerized acrylonitrile monomer in order to provide the container with the combination of chemical and physical properties which necessarily must be present in the thermoplastic in order that it be an effective material for packaging carbonated soft drinks and beer. Such polymerized monomer is preferably present at a level of from 60 to 80 weight percent in the polymer. In addition to relatively low oxygen and water permeability characteristics, acrylonitrile-based thermoplastics exhibit excellent tensile strength, e.g., between 8,000 to 11,000 psi in unoriented condition. The barrier effectiveness of nitrile-based polymers is dependent on the level of C-N groups therein and since the molecular weight of the repeating acrylonitrile unit in the polymer is lower by 20+ percent than that of the similar methacrylonitrile unit, less acrylonitrile by weight is required in a given polymer in comparison to that required for a related methacrylonitrile based polymer in order to obtain equivalent overall polymer barrier properties. Since these special high barrier polymers are expensive to synthesize, this represents a substantial advantage of the preferred acrylonitrile based materials over those based on methacrylonitrile. Methacrylonitrile, however, can be included in minor amounts in the polymer from which the bottles of the present invention are made — e.g., in packaging applications which are very oxygen sensitive and require extremely low transmission of oxygen.

Otherwise, any monomer or monomers which are copolymerizable with the acrylonitrile component of the polymer may be employed in the practice of this invention. The preferred range thereof is between 40 to 20 weight percent of the polymer. Exemplary of such monomers are the aforementioned methacrylonitrile, ethacrylonitrile, propacrylonitrile, alphachloroacrylonitrile, alpha-bromoacrylonitrile, alpha-fluoroacrylonitrile, alpha-cyano-styrene, vinylidene cyanide, alpha-cyano acrylic acids, alpha-cyano acrylates such as alpha-cyano methyl acrylates, alpha-cyano ethyl acrylates, and the like, 2,3-dicyanobutene-w, 1,2-dicyanopropene-1, alpha-methylene glutaronitrile, and the like. Also, ethylenically unsaturated aromatic compounds such as styrene, alpha-methyl styrene, ortho-, meta-, and para-substituted alkyl styrenes, e.g., ortho-methyl styrene, ortho-ethyl styrene, para-methyl styrene, para-ethyl styrene, ortho-, meta-, or para-propyl styrene, ortho-, meta-, or para-isopropyl styrene, ortho-, meta-, para-butyl styrene, ortho-, meta-, or para-

secondary butyl styrene, ortho-, meta-, or para-tertiary butyl styrene, etc., alpha-halogenated styrene, e.g., alpha-chlorostyrene, alpha-bromostyrene, ring-substituted halogenated styrenes, e.g., ortho-chlorostyrene, para-chlorostyrene, and the like; esters of ethylenically unsaturated carboxylic acids e.g., methyl acrylate, methyl methacrylate, ethyl methacrylate, ethyl acrylate, butylacrylate, propyl acrylate, butyl methacrylate, glycidol acrylate, glycidol methacrylate, and the like, ethylenically unsaturated acids, carboxylic acids such as acrylic acid, methacrylic acid, propacrylic acid, crotonic acid, citraconic acid, and the like. Vinyl esters, e.g., vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinyl and vinylidene halides, e.g., vinyl chloride, vinyl bromides, vinylidene chloride, vinylidene chloride, vinyl fluorides, etc.; vinyl ethers, e.g., methyl vinyl ether, ethyl vinyl ether, alpha-olefins, e.g., ethylene, propylene, butene, pentene, hexene, heptene, octene, isobutene, and other isomers thereof. A particularly preferred composition comprises 65-75 weight percent polymerized acrylonitrile, 35-25 weight percent polymerized styrene.

It is contemplated that conventional additives or modifiers such as dyes, fillers, pigments, plasticizers, stabilizers, etc., may also be used in the polymers from which the bottles of the present invention are made.

Referring now to the drawing, there is illustrated a one-piece, optionally disposable, bottle 10 for packaging a beverage such as a cola soft drink or beer under carbonation pressure. Bottle 10 comprises an axially symmetrical, generally cylindrical body 12 which includes sidewall 14 which may slope inwardly along its length toward the upper end as at 17 and which has a discharge opening 15 at such upper end. Means such as threads 19 are formed in sidewall 14 adjacent opening 15 for cooperating with a pressure-confining closure (not shown) such as a twist-off metal cap. Other forms of neck finish obviously may be employed. Sidewall 14, as illustrated particularly in FIG. 2, has a right cylindrical section adjacent its lower end.

Bottle 10 has a bottom portion generally indicated as 16 at the lower end of sidewall 14 which includes substantially toroidal segment 18 surrounding and integral with inwardly recessed inner base wall 20 and which preferably merges smoothly at its outermost end into the lower end of sidewall 14 and at its innermost end into inner base wall 20. Inner base wall 20 closes off the bottom of bottle 10 and preferably comprises curved portion 22 having a radius substantially equal to but reverse from that of segment 18. Wall 20 may have a centrally depressed portion 24 for accommodating the preferred process of forming bottle 10 to be described more completely hereafter. The maximum height 16 of inner base wall portion 20 above lowermost point 36 of segment 18 in the illustrated embodiment is no greater than and preferably is about equal to radius R of segment 18 plus the thickness of the plastic forming portion 20.

The radius of curvature R of segment 18 in order to achieve the purposes of the present invention must be between 10 to 20 and preferably 13 to 18 percent of the maximum diameter of generally cylindrical body 10, which maximum diameter is represented by D in the illustrated embodiment. Segment 18 should be present in the bottom portion at least to the extent of 30 and preferably 37 percent of that of a full torus, such imaginary remaining portion being illustrated in

FIG. 2 by dotted line 26. Thus, if a surface between 28-30 in FIG. 2 is considered to represent the area of one-half of a torus, portion 28-32 would represent 25 percent thereof and portion 28-34 about 37 percent thereof.

The polymer forming segment 18 of container 10 is molecularly oriented. The level of orientation through the thickness of the material will vary when the bottle is formed as hereafter described, generally being more oriented on or adjacent the outer surface and decreasing in orientation level through the thickness to the inner surface. The orientation as measured by the orientation release stress of the material, particularly in portion 28-32 of the toroidal segment, is at least 50 psi in the axial direction and at least 50 psi in the circumferential direction, such values representing the average through the thickness when the levels vary through such thickness as just described.

EXAMPLE

A heat plastified, 70/30 weight percent polymerized acrylonitrilestyrene copolymer was shaped by conventional means such as blow or injection molding into a closed bottom end, open top end tubular preform having means such as threads 19 formed thereon, the body of which is illustrated in outline form as 38 in FIG. 1. Preform 38 is brought to a temperature on the order of 280° F. by exposure to a suitable temperature conditioning medium, at which temperature substantial molecular orientation thereof occurs on stretching. The temperature range within which such orientation can be developed for the acrylonitrile-based polymers of the present invention has been found to be 250°-310° F. Preform 38 while at this temperature is then supported adjacent its open end between suitable cooperating sections of a conventional blow mold (not shown) whereupon stretch rod (FIG. 1) is introduced therein so as to force foot 42 against the closed bottom of the preform. Rod 40 is then caused to move by suitable conventional means toward the opposite closed end of the mold to substantially stretch the vertical walls of preform 38 and especially those portions adjacent the closed end, in the vertical direction to thereby develop substantial axial orientation in the plastic. When foot 42, with the closed end of the preform impaled on its outer surface, has reached the bottom of the blow mold and is preferably seated within a recess in the mold corresponding essentially to that of 24 in FIG. 2, suitable valving is actuated in a conventional manner so as to cause air under pressure to flow through passage 44 in stretch rod 40 into the axially stretched preform. The air expands and consequently thins and forces the plastic radially of the axial position in the direction of arrow 54 toward the corner portion of the mold cavity which is to define toroidal segment 18 of the container. Such movement develops radial or circumferential orientation, but the plastic at the same time is also forced further downwardly in the axial direction under the influence of the air pressure into the furthest reaches of the mold defining segment 18 in order to develop additional axial orientation. In forming to the surface defining segment 18, the plastic can be considered to move in the general angular direction of arrow 52 which direction has horizontal 48 and vertical 50 directional components. Thus, with this type of forming and with a mold corresponding to the configuration illustrated in FIGS. 1 and 2, the plastic of segment 18 is ini-

tially stretched substantially in the axial direction because of the initial motion of rod 40, whereupon the thus initially stretched plastic is thereupon moved outwardly and downwardly, such outward direction representing an additional stretch direction and such downwardly oriented stretching of the previously stretched plastic representing yet another orientation direction. The container thus formed is held in contact with cooled walls of the blow mold cavity in a conventional manner to set the thermoplastic whereupon the mold sections are separated and the container is discharged therefrom. The entire container forming process usually takes on the order of five seconds. As illustrated in FIG. 2, inner wall portion 20 of the bottom of the container is relatively thick with portion 24 being the thickest, in comparison with that forming toroidal segment 18 due basically to the aforesaid stretching pattern. The wall of toroidal segment 18, however, in addition to being well oriented is quite thin and thus well capable of resiliently absorbing impact forces but not so thin as to be deficient in the required barrier properties. The thickness of segment 18 when formed in this manner generally ranges between 12 to 60 mils overall and between 12 to 40 mils in portion 28-32 of segment 18, increasing toward 60 mils along portion 32-34.

Bottle 10 and others formed in the same manner were thereafter filled in a conventional manner with a chilled cola beverage at 3.9 volumes of CO₂ and a roll-on aluminum cap applied about threads 19 whereupon the temperature of the contents was allowed to increase to room temperature. The filled bottles were then dropped through a vertical column from a height of 3 feet onto a flat steel plate backed by concrete. The column was sized such that the angle of bottom impact, i.e., the extent to which a plane through 36 of segment 18 is raised above the horizontal, did not exceed 2°-3°. The percentage of bottles 10 passing such test without rupturing was found to be between 60 to 80 percent of those tested.

Similar bottles were manufactured and filled as above described and tested for creep which is a measure of strain relaxation with time of the polymer. The bottles are placed in an enclosure such as an oven, maintained at 100° F., under which condition the internal pressure of the container reaches 80-100 psig. The containers are allowed to remain at 100° F. for 24 hours, at which time they are removed and the overflow capacity thereof measured to determine creep (i.e., increase in volume over that existent when the bottles were empty) caused by the time-temperature stress condition. Creep in bottles 10 was found to be less than 6 percent and usually 4-5 percent.

Similar containers were manufactured in the manner just described and a sample portion of toroidal segment 18 between 28-32 as illustrated in FIG. 2 was cut therefrom for the purpose of measuring orientation release stress therein by optical birefringence measurement, which is an indication of the level of molecular orientation in the material. The bottle segment is first sprayed on the interior side with a reflective coating — typically aluminum paint. The portion to be studied is marked with a grease pencil and physically oriented so that its maximum stress direction coincides with the vertical axis of a reflection polariscope. The reflection polariscope is an instrument which analyzes polarized light and enables the determination of optical birefringence. Two readings are taken: one at normal incidence and

one at oblique incidence. These values of retardation R_n and R_o are used to calculate orientation release stress from the following equations:

1. $\sigma_1 = C/2t [\cos \phi (R_o - R_n \cos \phi)/\sin^2 \phi]$
2. $\sigma_2 = C/2t [R_o \cos \phi - R_n/\sin^2 \phi]$

where:

- σ_1 = orientation release stress in direction No. 1, psi
- σ_2 = orientation release stress in direction No. 2, psi
- C = orientation release stress optical constant, (psi-in/fringe)
- t = sample thickness, inches
- ϕ = oblique angle used for R_o , degrees
- R_n = retardation for normal incidence, fringes
- R_o = retardation for oblique incidence, fringes

This method is more completely described in the publication by Drucker, D.C., "Photoelastic Separation Of Principal Stresses By Oblique Incidence," Journal of Applied Mechanics, Trans. ASME, 65, pp. A156-160 (143).

The bottles when examined for orientation release stress levels according to the above procedure were always found to provide values of at least 50 psi in the axial and circumferential directions, sometimes reaching as high as 200 psi in the axial and 450 psi in the circumferential direction depending on the process conditions and the overall bottle diameter in the base area. It may be possible to increase these upper levels by decreasing the temperature at which the plastic is stretched and increasing the pressure of the air used to move the plastic down into the toroidal segment of the mold.

Distance 16 in FIG. 2 which represents the maximum inward extent of the recessed area of the bottom of the container adjacent toroidal segment 18 is important in the present invention. If such depth is excessive, the wall thickness of the material, especially that of portion 28-32 of segment 18, which is the furthest from the axis of the container becomes too thin, thus rendering the container borderline or unsatisfactory in terms of barrier properties or impact resistance. Also, as the height of portion 20 above lowermost point 36 is increased in the mold defining the container contour, the plastic will be stretched more in taking the shape of such surface and consequently the level of molecular orientation will increase. With acrylonitrile-based polymers, however, it has been observed that when these materials are stretched during formation of a container in the manner previously described, as stretching or molecular orientation increases so also does the creep characteristic of the material increase or, in other words, the tendency of the container to increase in size under pressure. Therefore, optimum properties are not obtained merely by stretching the plastic as much as possible in order to develop maximum orientation and therefore greatest impact resistance, because if the polymer is stretched too much under the forming conditions previously described, excessive creep or deformation of the bottom of the container will occur, and such is possible if the inner base portion 20 projects too far into the body of the container. Height 16 should be between 5 to 30 percent of the maximum diameter D of the bottle, and is preferably maintained approximately equal to R (plus the wall thickness of the material). With such configurations, adequate orientation to develop the impact strength required in a pressurized beverage container is obtained without excessive creep

occurring subsequently after the container is pressurized. Described alternatively, the surface area of segment 18 from a point midway between 28-32 to 34 (FIG. 2) plus inner wall portion 20 should be on the order of 20-30 percent greater than that of the cross sectional area of an imaginary planar circle through lowermost point 36 in FIG. 2.

Also, the tensile strength of the acrylonitrile-based material is increased when molecularly oriented in the manner previously described to a value on the order of 10,000 psi to 20,000 psi. Thus, though radius R in FIG. 2 is relatively small in comparison with r in FIG. 1 for the prior art configuration, the increase in tensile strength of the material obtained by molecular orientation more than compensates for the sharper contour of segment 18, which contour allows development of the aforementioned orientation. In this manner, strength in the high stressed corner area of the bottle to withstand stress generated by the pressure of the contents is balanced with toughness to withstand impact during processing and use of the container by the consumer.

When bottles formed from the same polymer and in the same manner as just described except that the large radius, prior art base configuration such as that illustrated in 46 in FIG. 1 was used, the material in the chime area or juncture between the base and side wall was found to be essentially unoriented in comparison with that obtained with the configuration of the present invention. This is due in large part because of the reduced distance available for stretching in both the radial and axial directions during final forming. More specifically, the radial distance from the axis of the container to the chime area (r in FIG. 1) or the just described surface area of the overall base area which is covered by the material after expansion is substantially reduced over that in FIG. 2 and there likewise is a much reduced axial component generated in stretching the plastic off the centerline of the mold during final blowing. In addition, because of the inwardly decreasing contour of r in FIG. 1, the material forming to a corresponding mold surface will be thicker than that in a comparable area in FIG. 2, and therefore for a given mold surface temperature it will take longer to set the thicker thermoplastic. Since it has been found that initially developed orientation relaxes with time at temperature, though some orientation may be developed during final expansion with large radius configurations such as that of FIG. 1, such thickened hot wall sections mitigate against retaining it. Thus, though such prior art lower body portions utilizing generous radii are desirable to minimize stress buildup, adequate stretching of the plastic in the chime area for the purpose of generating molecular orientation cannot be obtained in forming such containers.

Various modifications and alterations will be readily suggested to persons skilled in the art. It is intended, therefore, that the foregoing be considered as exemplary only and that the scope of the invention be ascertained from the following claims.

What is claimed is:

1. A bottle for a beverage under pressure formed of a polymer wherein the major constituent is polymerized acrylonitrile monomer, said bottle comprising:
 - a. a generally cylindrical body which includes a side-wall portion having a discharge opening at its upper end and means formed therein adjacent said open-

ing for cooperating with a pressure-confining closure;

- b. a bottom portion at the other end of the sidewall portion comprising a substantially toroidal segment between the sidewall and an inner base wall surrounded by and integral with said toroidal segment and closing off the bottom portion of the bottle, the radius of curvature of said toroidal segment being between 10 to 20 percent of the maximum diameter of the generally cylindrical body, the surface area of said toroidal segment being at least 30 percent of that of a full torus, said toroidal segment having a varying overall wall thickness within a range of between 12 to 60 mils, said thickness gradually increasing within such range along said toroidal segment toward said inner base wall; and
- c. the polymer in at least a portion of said segment being molecularly oriented exhibiting an orientation release stress of at least 50 psi in both the axial and circumferential directions.

2. The bottle of claim 1 wherein said polymer comprises 60-80 weight percent polymerized acrylonitrile and 40-10 weight percent of at least one other monomer copolymerized therewith.

3. The bottle of claim 1 wherein said polymer includes as minor constituents polymerized methacrylonitrile monomer plus at least one other copolymerized

monomer.

4. The bottle of claim 1 wherein the inner base wall has a curved portion having a radius substantially equal to but reverse from the radius of curvature of the toroidal segment, said curved portion merging into said segment.

5. The bottle of claim 1 wherein the height of the inner base wall above the lowermost surface of the toroidal segment is between 5 to 30 percent of the greatest diameter of the bottle.

6. The bottle of claim 1 wherein the orientation release stress of said toroidal segment is between 50 to 200 psi in the axial direction and between 50 to 450 psi in the circumferential direction.

7. The bottle of claim 2 wherein styrene is the other copolymerized monomer.

8. The bottle of claim 3 wherein styrene is the other copolymerized monomer.

9. The bottle of claim 1 wherein said sidewall portion has a right cylindrical section at its lower end joined to said toroidal segment.

10. The bottle of claim 1 wherein said toroidal segment has an unchanging radius forming the radius of curvature thereof.

11. The bottle of claim 1 wherein said inner base wall has a central depressed portion therein.

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