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LAMINATED HYPODERMIC SYRINGE AMPUL

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This invention relates to hypodermic springe ampuls of the self aspirating type having a pierceable wall to be pierced by the rear end of a double-ended cannula of the hypodermic syringe wherein the ampul is to be used.

Of course, it is desired that the walls of ampuls of this class are impermeable to water vapour to the highest possible extent, so that any evaporation of the medical or therapeutic aqueous liquid content of the ampul is effectively prevented. Also, it is necessary that the walls of the ampul are highly impermeable to gases, especially oxygen, because it has been found that even traces of oxygen if allowed to penetrate the ampul walls from the atmosphere may destroy the medical or therapeutic effect of certain substances. Furthermore, it is desired that the ampul wall when pierced by the cannula shall form a substantially fluid-tight seal with the exterior surface of the cannula. Finally ampuls of the above mentioned kind as already indicated are required to exhibit an ability to aspirate, that is an ability to resume their normal form when relieved from a momentary compression force, and thereby to suck back some of the expelled content thereof in mixture with some blood to indicate the proper penetration of the cannula point into a vein, for instance.

Efforts have been made to produce hypodermic syringe ampuls which would meet the above discussed requirements. Thus, a wide variety of single layer homogeneous materials have been tried in attempts to provide for the desired gas and water vapour barriers. Thereby, it has turned out that material which provide for the desired gas and water vapour barriers are unable to render the ampul aspirating. Certain other materials render the ampul aspirating but then the impermeability to either gases or water vapour may fail or are such materials unable to provide for the necessary fluid-tight seal with the exterior surface of the cannula. Certain ampuls with gas and water vapour impermeable walls and having a satisfying aspirating ability hav been proposed but then the aspirating ability is based on the particular shape of the ampul rather than on the inherent elasticity of the wall material of such ampul. Evidently, such particular shapes of the ampuls are associated with higher manufacturing costs as well as increased space demands. Furthermore, it should be noted that certain such prior ampuls rely on the gripping action of the material of the ampul walls against the exterior of the cannula for forming the fluid-tight seal with said cannula when this pierces the ampul wall. Thus, the ampul wall must have an inherent ability to exert a rather considerable sealing pressure against the cannula, which is commonly associated with some difficulties for the cannula to pierce the wall.

The primary object of the present invention is to provide an entirely reliable self aspirating ampul by which the above mentioned requirements are fully met at the same time as the indicated drawbacks of the prior art ampuls are overcome. To this end, the self-aspirating hydrodermic syringe ampul according to the invention, having a pierceable wall to be pierced by the rear end of a double ended cannula of the hypodermic syringe wherein the ampul is used, is characterized essentially in that it is made of a laminated material consisting of at least two layers of plastic bonded together by means of an adhesive agent being present in an amount of 3 to 20

g./m.^{2} (i.e. grams per square meter), the first one of said layers having a permeability to gases of less than 5.0 mg.mm./m.^{2}.24h.cm. Hg (i.e. milligrams of gas penetrated in 24 hours per square meter of area through a layer of 1 millimeter thickness under a pressure differential of 1 centimeter of mercury), and to water vapours of less than 400 mg.mm./m.^{2}.24h.cm. Hg, and the second one of said layers having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} (i.e. kilograms per square centimeter) as well as a thickness great enough to give the ampul an aspirating force of at least 0.1 kg./cm.^{2} solely due to the inherent elasticity of said second layer in combination with the elasticity of said first layer, if any.

Preferably, said first layer of the laminate material has a permeability to gases of less than 1.0 mg.mm./m.^{2}. 24h.cm. Hg and permeability to water vapours of less than 200 mg.mm./m.^{2}.24h.cm. Hg, whereas the modulus of elasticity of said second layer preferably is within the limits of 35,000 to 45,000 kg./cm.^{2} when said layer has a thickness to give the ampul an aspirating force of at least 0.1 kg./cm.^{2} at such modulus of elasticity.

The laminated material used for the walls of the ampul according to the invention may comprise three layers of plastic, the inner layer of such laminated material having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} and a thickness great enough to give the ampul an aspirating force of the above mentioned order, the outer layers together having permeabilities to gases and water vapour not exceeding the above mentioned values, and at least two of said three layers being bonded together by means of an adhesive agent being present in an amount of 3 to 20 g./m.^{2}.

In the manufacture of ampuls of the above mentioned kind it is commonly desirable to start with forming a tube having a longitudinal seam in the form an overlap joint. Thereby, it is preferred that the opposing superficial layers of the superposed edge portions of the laminated material are of the same composition in order to permit heat sealing of the overlap joint. To this end, it is often preferred to use a three-ply laminated material wherein both superficial plies are of the same composition.

For certain applications it may be found desirable when using a laminate material with three or more layers to concentrate the different permeabilities to different layers of the material. Thus, one of the superficial layers, for instance, may have a permeability to gases not exceeding 5.0 mg.mm./m.^{2}.24h.cm. Hg, and preferably less than 1.0 mg.mm./m.^{2}.24h.cm. Hg, whereas the other superficial layer, for instance, has a permeability to water vapour of less than 400 mg.mm./m.^{2}.24h.cm. Hg, and preferably less than 200 mg.mm./m.^{2}.24h.cm. Hg.

With a laminated material comprising three or more layers it is, of course, possible to bind together two of such layers without using any adhesive agent between them. In this case, it is possible to extrude one of the layers onto one of the other ones of the laminated material in the form of a liquid solution containing a solvent which is evaporated so that the solute residue forms the extruded layer. It is also possible to melt one layer onto one of the other layers to form the laminated material.

Examples of material of suitable rigidity to enable aspiration are nonplastified polyvinyl chloride, polytriflour monochloroethylene, polyethyleneterephthalate, polyamide -6,6, and polyvinyl fluoride.

Examples of materials that secure the desired water vapour impermeability are polyethylene, types LD, MD, HD, polypropylene, rubber hydrochloride, polytrifluormonochloroethylene, and polyvinylidene chloride.

Examples of materials that secure the desired gas impermeability are polyethyleneterephthalate, polycarbon-

ate, polyamide-6,6, polytrifluormonochloroethylene, polyvinylidene chloride, and nonplastified polyvinyl chloride.

It has been found that the adhesive agent contributes considerably in providing for the desired fluid-tight seal, and it has further been ascertained that for this reason a material should be used which maintains its adhering properties for a rather extended period. Examples of such materials are butyl rubber, nitrile rubber, chlorinated polyethylene, and, polyisobutylene.

Preferred laminated materials to be used for ampuls according to the invention are set forth in the following non-limiting examples:

Example 1

Material:	Thickness in millimetres
Polyethyleneterephthalate	0.1
Polyisobutylene	0.002 to 0.003
Polyvinylidene chloride	0.06
Total	0.16

The laminated material has the above mentioned layers which exhibit a modulus of elasticity of 34,000 kg./cm.^{2}, a permeability to water vapour of 16.7 mg.mm./m.^{2}.24h. cm. Hg, and a permeability to oxygen of 0.0004 mg.mm./m.^{2}.24h.cm. Hg.

Example 2

Material:	Thickness in millimetres
Polyethyleneterephthalate	0.1
Polyethylene (type LD)	0.03
Polyisobutylene	0.002 to 0.005
Polyvinylidene chloride	0.05
Total	0.18

The laminated material has the above mentioned layers which exhibit a modulus of elasticity of 32,300 kg./cm.^{2}, a permeability to water vapour of 13.1 mg.mm./m.^{2}.24h. cm. Hg, and a permeability of 0.0004 mg.mm./m.^{2}.24h. cm. Hg to oxygen.

Example 3

Material:	Thickness in millimetres
Rubber hydrochloride P4–120	0.15
Polyisobutylene	0.002 to 0.003
Polyethyleneterephthalate	0.10
Polyisobutylene	0.002 to 0.003
Rubber hydrochloride P4–120	0.15
Total	0.40

The laminated material has the above mentioned layers which exhibit a modulus of elasticity of 11,200 kg./cm.^{2}, a permeability to water vapour of 35.2 mg.mm./m.^{2}.24h. cm. Hg, and a permeability of 0.0005 mg.mm./m.^{2}.24h. cm. Hg to oxygen.

Example 4

Material:	Thickness in millimetres
Polyvinylidene chloride	0.03
Polyisobutylene	0.002 to 0.003
Non-plastified polyvinyl chloride	0.10
Polyisobutylene	0.002 to 0.003
Polyvinylidene chloride	0.03
Total	0.16

The laminated material has the above mentioned layers which exhibit a modulus of elasticity of 33,600 kg./cm.^{2}, a permeability to water vapour of 9.6 mg.mm./m.^{2}.24h. cm. Hg and a permeability of 0.001 mg.mm./m.^{2}.24h.cm. Hg to oxygen.

It has been ascertained that ordinary hypodermic syringe ampuls having walls of the laminate materials as exemplified above exhibit an aspirating force within the limits of 0.1 to 0.2 kg./cm.^{2}.

What we claim is:

1. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypodermic syringe which comprises at least two layers of a plastic material with an adhesive agent therebetween; at least one of said plastic layers having a permeability to gases of less than 5.0 mg.mm./m.^{2}.24h.cm.Hg; at least one of said plastic layers having a permeability to water vapor of less than 400 mg.mm./m.^{2}.24h.cm. Hg; at least one of said plastic layers having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} and a thickness sufficient to provide an aspirating force of at least 0.1 kg./cm.^{2} to the ampul solely due to the elasticity of said layers; said adhesive agent being at least 3 g./m.^{2} to provide a seal with an external surface of the cannula and to bond said plastic layers.

2. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypodermic syringe; said wall comprising a first layer of plastic material having a permeability to gases of less than 5.0 mg.mm./m.^{2}.24h.cm. Hg and having a permeability to water vapor of less than 400 mg.mm./m.^{2}.24h.cm. Hg; a second layer of plastic material having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} and a thickness sufficient to provide an aspirating force of at least 0.1 kg./cm.^{2} to the ampul solely due to the elasticity of said layers; and an adhesive layer between said first and said second layers being at least 3 g./m.^{2} to provide a seal with an external surface of the cannula and to bond said first and second layers.

3. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypodermic syringe which comprises an outer layer; an inner layer; and an adhesive layer between said outer and said inner layers; said outer layer having a permeability to gases of less than 5.0 mg.mm./m^2.24 h.cm. Hg and having a permeability to water vapor of less than 400 mg.mm./m.^{2}.24h.cm. Hg; said outer layer being a plastic material selected from the group consisting of polyethylene, polypropylene, rubber hydrochloride, polytrifluormonochloroethylene, polyvinylidene chloride, polyethylene terephthalate, polycarbonate, polyamide-6,6 and nonplastified polyvinyl chloride; said inner layer having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} and a thickness to provide an aspirating force of at least 0.1 kg./cm.^{2} to the ampul; said inner layer being a plastic material selected from the group consisting of polyvinyl chloride, polytrifluormonochloroethylene, polyethylene terephthalate, polyamide-6,6 and polyvinyl chloride; said adhesive layer being at least 3 g./m.^{2} to provide a seal with an external surface of the cannula end and to adhere said inner layer to said outer layer; said adhesive layer being selected from the group consisting of butyl rubber, nitrile rubber, chlorinated polyethylene, and polyisobutylene.

4. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypodermic syringe which comprises a polyethylene terephthalate inner layer with a thickness of 0.1 mm.; a polyvinylidene chloride outer layer with a thickness of 0.06 mm.; a polyisobutylene adhesive layer between said inner and outer layers with a thickness of 0.002 to 0.003 mm. and with 3 to 20 g./m.^{2}; said adhesive layer providing a seal with an external surface of the cannula; said ampul having in its layers a modulus of elasticity of 34,000 kg./cm.^{2}, a permeability to water vapor of 16.7 mg.mm./m.^{2}.24h.cm. Hg and a permeability to oxygen of 0.0004 mg.mm./m.^{2}.24h.cm. Hg.

5. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypo-

dermic syringe which comprises an outer layer; a middle layer; an inner layer; and an adhesive layer; said outer layer having a permeability to gases of less than 5.0 mg.mm./m.^{2}.24h.cm. Hg; said middle layer having a permeability to water vapor of less than 400 mg.mm./m.^{2}.24h.cm. Hg; said inner layer having a modulus of elasticity of 10,000 to 75,000 kg./cm.^{2} and a thickness sufficient to provide an aspirating force of at least 0.1 kg./cm.^{2} to the ampul solely due to the elasticity of said layers; said adhesive layer being at least 3.0 g./m.^{2} to provide a seal with an external surface of the cannula and to bind at least two of said outer, inner and middle layers.

6. A laminated hypodermic syringe ampul of the self-aspirating type having a wall capable of being pierced by the rear end of a double-ended cannula of the hypodermic syringe which comprises a polyvinylidene chloride outer layer with a thickness of 0.005 mm.; a polyethylene middle layer with a thickness of 0.03 mm.; a polyethylene terephthalate inner layer with a thickness of 0.1 mm.; and a polyisobutylene adhesive layer with a thickness of

0.002 to 0.005 mm. and with 3 to 20 g./m.^{2} to provide a seal with an external surface of the cannula and to adhere said outer layer to said middle layer; said ampul having in its layers a modulus of elasticity of 32,300 kg./cm.^{2}, a permeability to water vapor of 13.1 mg.mm./m.^{2}.24h.cm. Hg and a permeability to oxygen of 0.0004 mg.mm./m.^{2}.24h.cm. Hg.

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