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(54) Title: PNEUMATIC TIRE HAVING MULTIPLE BUILT-IN SEALANT LAYERS AND PREPARATION THEREOF

(57) Abstract: A tire with a built-in puncture sealant comprises a supporting tire carcass comprised of one or more layers of ply, an outer circumferential tread (120), and a radially inner layer, a pair of beads (113), sidewalls extending radially inward from the axial outer edges of the tread (120) portion to join the respective beads (113), a sealant comprising an outer layer of sealant (102) and an inner layer of sealant (101), disposed inwardly from said tire carcass inner layer, wherein the outer layer of sealant (102) and the inner layer of sealant (101) have different viscosities, and wherein said sealant provides self-sealing properties to the tire.

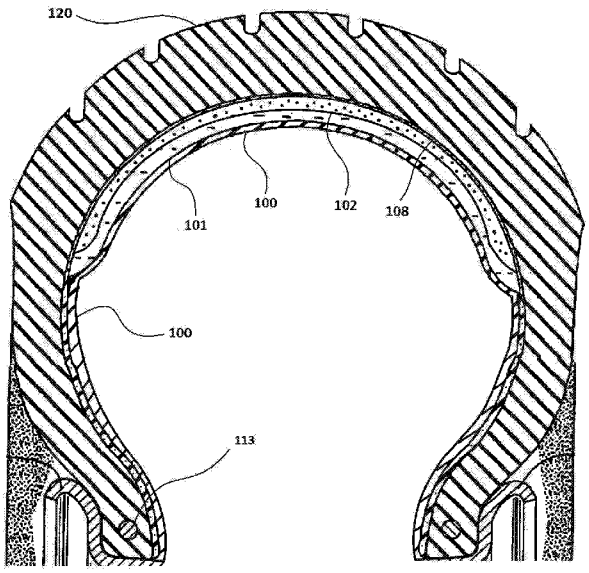


Fig. 2

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PNEUMATIC TIRE HAVING MULTIPLE BUILT-IN SEALANT LAYERS AND PREPARATION THEREOF

BACKGROUND OF THE INVENTION

The present invention is directed to tires having inner sealant layers, and in particular to tires with multiple built-in sealant layers where at least one of them is formed from sealant precursor layers.

Tire puncture is an inherent issue for rubber tires. Because of that, sealants have been developed and placed in the inner tire to minimize the impact on the puncture. Further, punctures can occur at any temperature. A single layer of sealant of low viscosity may work very well at low temperature, but at high temperatures, it might achieve a very low viscosity, which would allow it to flow and pass out of tire during use. By depleting the tire sealant, the tire looses its puncture sealing capacity. Likewise, a single layer of sealant of high viscosity may be very good for high temperature but might be almost solid at cold temperature and thus unable to flow to plug puncture in tires at cold temperature.

Tires with built-in sealant layer are known in the art. Typically, these tire sealants are peroxide containing butyl-rubber-based sealant precursor layers, such as for example, US Patent Nos. 4,895,610; 6,962,181; 7,073,550; 7,674,344; and 8,293.049; and US Patent Publication Nos. 2005/0113502 and 2005/021568, the teachings of which are all hereby incorporated by reference. Sealant layers may be of black or non-black colors and may incorporate short fibers, such as polyester or polyurethane fibers, and other filler aggregate into sealant layers to help to plug nail hole punctures.

Tires using multiple layers are known, such as US Patent No. 8,387,672 to Majumdar where multiple layers are used and the layers are based on polyurethane sealant precursor where a non-woven layer is incorporated into it. The teaching is that the non-woven material is used to prevent leakage of polyurethane sealant plugs the puncture.

BRIEF SUMMARY OF THE INVENTION

A tire with a built-in puncture sealant comprising a supporting tire carcass comprised of one or more layers of ply, an outer circumferential tread, and a radially inner layer, a pair of beads, sidewalls extending radially inward from the axial outer edges of the tread portion to join

the respective beads, a sealant comprising an outer layer of sealant and an inner layer of sealant, disposed inwardly from said tire carcass inner layer, wherein the outer layer of sealant and the inner layer of sealant have different viscosities, and wherein said sealant provides self-sealing properties to the tire.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other features and advantages of the present invention will become apparent to those skilled in the art to which the present invention relates upon reading the following description with reference to the accompanying drawings, in which:

Fig. 1 is a cross-sectional view of the sealant and sealant cover layers;

Fig. 2 is a cross-sectional view of a tire using the present invention;

Fig. 3 is a cross-sectional view of a tire showing an alternate embodiment of the present invention;

Fig. 4 is a cross-sectional view of a tire showing an alternate embodiment of the present invention;

Fig. 5 is a partial cross-sectional view of a punctured tire and illustrating the prior art;

Fig. 5A is a partial cross-sectional view of a punctured tire and illustrating the prior art;

Fig, 6 is a partial cross-sectional view of a punctured tire using the present invention;

Fig. 7 is a cross-sectional view of a tire showing an alternate embodiment of the present invention; and

Fig. 8 is a cross-sectional view of a tire showing yet another alternate embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a tire with a plurality of built-in sealant layers. The tire comprises a supporting tire carcass comprised of one or more layers of ply, an outer circumferential tread, and a radially innermost layer, a pair of beads, sidewalls extending radially inward from the axial outer edges of the tread portion to join the respective beads, a sealant layer comprising an inner liner, two or more layers of sealants, and a cover layer, disposed on said tire carcass innermost layer, wherein said inner liner is affixed to said tire carcass innermost layer, wherein the two or more layers of sealants are disposed between said inner liner and said cover

layer, wherein the two or more layers of sealants comprise an inner layer and an outer layer and have different viscosities, wherein said sealant layer provides self-sealing properties to the tire.

The order of the layers of the tire anatomy, from outmost to innermost comprises: outermost layer is the tread layer, followed by a traditional tire carcass (including ply and belts), then an inner liner, the outer sealant layer, the inner sealant layer, and a protective cover layer as the innermost layer. An optional gas permeable layer can be disposed between the inner liner and the innermost layer of the tire carcass. The inner liner is permanently affixed, bonded, or joined to the inner surface of the tire carcass. The outer and inner sealant layers are used in reference to one another's relative position and are part of the internal structure of the tire. I.e. the outer sealant layer is not located on, or part of, the exterior/outside of the tire.

The present invention uses a sealant comprising a plurality of built-in puncture sealant layers in the form of an outer sealant layer and an inner sealant layer. The use of a plurality of layers provides much better performance than tires with one layer of sealant of equivalent total thickness. With the present invention, better puncture sealing efficiency is achieved when the outer sealant layer is the high viscosity sealant layer and the inner sealant layer is the low viscosity sealant layer (i.e. the high viscosity sealant layer is closer to the outer surface of the external tire tread, and the low viscosity layer is closest to center of the tire/the axis of rotation of the tire). The inner and outer sealant layers comprise predominantly degraded butyl rubber.

As used herein, the term "sealant precursor" means the compound by itself is not a sealant, but it is transformed into sealant by thermal degradation during high temperature tire cure step used in making the tire. The "precursor layer(s)" is the layer of sealant precursor. The precursor layer can be 100% butyl rubber or predominantly butyl rubber, comprising 80%-90% butyl rubber and can include up to approximately 5% diene-based elastomer. Butyl rubbers degrade during tire curing at high temperature to form low molecular weight tacky sealants. Multiple sealant layers can be placed inner to the tire inner liner where a sealant protective layer is applied to prevent fouling of tire curing bladder. Multiple sealant layers can also be sandwiched between tire inner liner and tire casing where no sealant protective layer is needed since the tire inner liner prevents bladder fouling. However, a squeegee layer is necessary between ply and sealant layer to prevent sealant travelling between the cords to the plies.

Any rubber based composition, such as natural rubber, butadiene rubber, styrene-butadiene rubber based composition, can be used for squeegee layer. For convenience, the

composition of squeegee layer may be same as inner liner layer, however, the thickness should be much smaller as barrier property is not needed. Typically, squeegee layer should be less than 1 mm and between 0.5 – 1 mm. Thickness of conventional halo-butyl rubber-based inner liner layer should be around 1.5 mm for passenger tire and up to 4 mm for bigger tires, such as truck tires.

The low viscosity/inner sealant layer, has very low storage modulus (G') and it cannot be calendered or conveniently applied directly during tire building. To compensate for this, the build starts with a higher G' sealant precursor layer that degrades *in-situ* during tire cure, catalyzed by appropriate peroxide (discussed below), thus forming the lower G' sealant layer. Similarly, higher viscosity/outer sealant layer can be formed *in-situ* from sealant precursor layer. However, higher viscosity sealant layer has high enough G' to be applied directly during tire building without the need of thermal degradation by peroxide. The differing viscosities are achieved by varying or withholding the amount of peroxide.

A barrier layer, either the inner liner (*see* Fig. 2) or squeegee layer (*see* Fig. 3), is used to keep the sealants from being absorbed by fibrous material that reinforced tire tread. Such a layer is desired but not believed to be critical.

Any commercially available butyl rubber can be used as sealant precursor layer. A variety of butyl rubber with unsaturation levels 0.90 – 2.25 mol % and Mooney Viscosity (ML(1+8) 125°C) in the range 33 – 51 MU (Mooney Units), such as are available from Lanxess, can be used. By heat in the presence of peroxide catalyst, butyl rubber degrade to lower Mooney Viscosity (ML(1+8) 125°C) rubber with range in between 5 -25 MU.

Besides butyl rubber, other rubbers that degrade by peroxide can be used as sealant precursor either alone or in combination with butyl rubber. One example of such rubber is brominated isobutylene-isoprene copolymer, available as X_BUTYL™ I4565P from Lanxess, can be used. This polymer has Mooney Viscosity (ML(1+8) 125°C) in the range 52 – 60 MU. By heat in the presence of peroxide catalyst, X_BUTYL™ I4565P rubber degrade to lower Mooney Viscosity (ML(1+8) 125°C) rubber with range in between 10 -35 MU.

The higher viscosity sealant layer is predominantly composed of butyl rubber, brominated isobutylene-isoprene copolymer, and combinations thereof. It has a Mooney viscosity (ML(1+8) 125°C) in the range 25 – 60 MU, so long as it has higher viscosity than the

lower viscosity layer. (For example, if the high viscosity layer was 25 MU, the lower viscosity layer would have to be 24 MU or less.)

The present invention employs a standard tire-building process. After the green (uncured) tire is built, an optional protective film can be applied on the top of the innermost layer. The width of the film is slightly wider than the sealant layer (approximately 2 inches more on both sides). This film protects the tire curing bladder and keeps it clean in case the innermost sealant cover layer ruptures or tears in the mold. Such films are known in the art. One such film is 2 mil undrawn nylon 6, 6 available as DARTEK® C900 from Coveris High Performance Packaging. About 1" (inch) of the film is overlapped at the end so that, after tire cure, it functions as a pull tab to facilitate easy removal. Such a system is described in US Patent No.7,332,047 to Majumdar, Logan, and Lukich, and is hereby incorporated herein by reference. The protective film can also be applied as first layer in tire building drum. For convenience, the two edges of the film are preferentially coated with a pressure-sensitive adhesive (PSA)-coated thermoformable film. Such a system is described in US Patent No.7,419,557 to Majumdar and Page, and is hereby incorporated herein by reference. Although the film is not critical, Dynamically Vulcanized Alloy (DVA) film is preferred in tire building drum over nylon-6,6 film because DVA has significantly lower low strain modulus and hence can expand using less forces. Such a material is described in US Patent No. 8,776,851 to Majumdar, and is hereby incorporated herein by reference. Other examples are US Patent Nos. 8,021,730 and 8,158,721. An activating agent for organoperoxide can be added in the sealant composition for faster degradation. Such a method is described in US Patent No. 7,674, 344 to D'Sidocky et al., and is hereby incorporated herein by reference.

The present invention incorporates an inner liner and sealant precursors. The inner liner comprises bromobutyl rubber, carbon black, naphthenic oil, stearic acid, phenolic resin tackifier, mixture of dark aromatic hydrocarbon resins (as found in STRUKTOL® 40 MS resin, manufactured by Struktol Company of America), MgO, ZnO, Sulfur, 2,2'-dithiobis(benzothiazole) (commonly sold as MTBS). The sealant precursors comprise butyl rubber, bromobutyl, polybutadiene, paraffinic oil, silica, clay, titanium dioxide, talc, phthalo/diarylide color concentrate dye/pigment (such as AKROSPERSE® E2295 Green manufactured by Akrochem Corporation), orange pigment (such as AKROSPERSE® E6615 Orange manufactured by Akrochem Corporation), blend of fatty acid derivatives processing

additives (such as STRUKTOL® HPS 11 processing additive manufactured by Struktol Company of America), in the first non-productive (NP) mixing pass. Organic peroxide, such as n-butyl 4,4-bis(t-butyl-peroxy)valerate (such as TRIGONOX® 17-40B-GR manufactured by AkzoNobel) can be added in the final productive (PR) pass.

Preferably the tire of the present invention is prepared in the following way:

1. A sealant cover layer having formulation shown in Table 1 is mixed and calendered to a thickness of 1 mm, and a width equal to the inner liner width.
2. A precursor for low viscosity sealant having formulation shown in Table 2 is mixed and calendered to a thickness of 3 mm thick, and a width equal to the tread width less about 15 mm (i.e., tread width *minus* 15 mm).
3. Next, a precursor for high viscosity sealant having the formulation shown in Table 2 is mixed and calendered to a thickness of 3 mm thick and a width equal to tread width.
4. The sealant cover layer (#1 above) is applied to the tire building drum.
5. Next, the precursor for low viscosity sealant (#2 above) is applied to the tire building drum.
6. Next, the precursor for high viscosity sealant (# 3 above) is applied to the tire building drum.
7. Next, the inner liner is applied in a tire building drum as in typical tire building process followed by the rest of the layers employed in a normal tire build.

An alternate embodiment comprises following the steps noted above, but modified such that instead of using low and high viscosity sealant layers, use a three or more intermediate layers of intermediate viscosities.

Table 1
Secalant cover layer

Ingredient	Parts per Hundred Rubber (PHR)
Bromobutyl rubber	100
Carbon black	55
Naphthenic Oil	6
Stearic Acid	1
Phenolic resin tackifier	4
STRUKTOL® 40 MS Resin	8
MgO	0.15
ZnO	2.0
Sulfur	0.5
MBTS (2,2'-Dithiobis(benzothiazole))	1.5

Table 2
Two sealant precursors

		4C014A	4C014B
Component	***Stage***	***Viscosity after sealant formation***	
		Low	***High***
Butyl Rubber	NP	100.00	100.00
Bromobutyl		5	0
Polybutadiene		-	5
Paraffinic oil	NP	13.00	13.00
Silica	NP	20.00	20.00
Clay	NP	10.00	10.00
Titanium Dioxide	NP	2.0	2.0
Talc	NP	0.5	0.5
AKROSPERSE® E2295 Green	NP	1.0	-
AKROSPERSE® E6615 Orange	NP	-	1.00
STRUKTOL® HPS 11		2	2
n-butyl 4,4-bis(t-butyl-peroxy)valerate	PR	12	6
TOTAL		**165.5**	**159.5**

For ease of illustration, some internal materials of the tire have been omitted from some of the drawings, such as belts and plies, but they remain in the finished tire.

Referring now to Fig. 1, which is a simplified illustration of the sealant and sealant cover layers, where the layers are not shown to scale since it is the ordering of the layers, not the specific widths and thicknesses that is important. The width can range from full tire width, down to a small strip along the center of the tire. A first sealant precursor layer **101'** and second sealant precursor or direct sealant layer **102'** and sealant cover layer **100'** are shown in a general form. In a preferred embodiment, the inner sealant precursor layer **101'** forms lower viscosity than the outer layer **102'**. During a puncture, the sealants **101**, and/or **102** (See Fig. 6) flow into the hole, filling it. The cover layer **100** may stretch and cover/plug the hole from the inside of the tire depending on tire internal temperature and diameter of puncture.

Fig. 2 shows sealant layers of Fig.1 in a tire. Low viscosity inner layer of sealant **101**, and high viscosity outer layer of sealant **102** (formed from precursor layers **101'**, **102'**, respectively, *see* Fig. 1) are inner to inner liner **108**, (i.e. closer to the tire's center) and a sealant cover layer

100 is needed. Cover layer **100** extends the width of the tire to the beads **113**. The outermost layer is the tire tread **120**. Optionally a nylon film (not shown) can be placed inner to sealant cover layer and covering the sealant layer underneath the sealant cover layer. The purpose of the nylon film is to prevent sealant leakage in case of crack in sealant cover layer. The nylon film would need to be removed after the tire is cured.

Fig. 3 is an alternate embodiment of the tire depicted in Fig. 2. In this embodiment, the inner liner **108** is inner to the sealant layers **101**, **102**. This arrangement requires a squeegee layer **109**, as discussed above.

Fig. 4 shows an alternate embodiment of the present invention wherein the sealant layers **101**, **102** are embedded into the tire, such that the cover layer **100** is flush with the inside of the tire. Sealant is composed of butyl rubber which is also a good barrier, so an additional inner liner layer underneath the sealant is not needed. Such an arrangement results in material saving and lower weight tire.

A single layer of sealant of low viscosity may be good for low temperature but at high temperature it may leak out, as shown in Fig. 5. High temperatures reduce the viscosity of the sealant layer **301**, such that it could cause leakage **302** through the tire puncture opening **300** and eventually run out of tire during use, thus impairing nail hole sealing capability. This would also contaminate roadways. Likewise, a single layer of sealant of high viscosity may be very good for high temperature and the same sealant may be almost solid at cold temperature and cannot flow to plug puncture in tires at cold temperature, as shown in Fig. 5A. Low temperatures increase the viscosity of the sealant layer **301**, such that it does not flow, or flows only slightly, creating minimal sealant bulges **303**, leaving an air gap and failing to seal the tire puncture opening **300**.

In typical puncture sealing tires, such as GOODYEAR DURASEAL® tires, e.g. US4,895,610, US4359078, US6,962,181, USPP 2005/0113502, 2005/0215684 the sealant layer sandwiched between thick inner liner and casing. In this case, the inner liner is very thick and cannot stretch and plug the punctures.

As shown in Fig. 6 one of the embodiments of the present invention uses a sealant layer that is inner to inner liner **108** and protected with low modulus thin sealant cover layer **100**. When a puncture occurs, the high viscosity layer **102** and low viscosity layer **101** flow into the puncture hole **300**. This creates a sealant plug **202**, which prevents deflation. Further, depending

on temperature and puncture hole diameter the protective layer **100** may stretch and plug big tire punctures permanently.

Fig. 7 shows an alternate embodiment of the present invention where sealant layers **101**, **102**, are in two separate compartments which will reduce sealant movement during tire use. In other words, the sealant is split into two or more parallel circumferential bands. Likewise, sealant layers can be in four compartments, as shown in Fig. 8, where the two or more parallel circumferential bands from Fig. 7 comprise four bands. Generally nails enter through tread grooves and the attachment of sealant cover or inner liner should be underneath tread lug. This will reduce the overall amount of sealant needed in a tire.

The following examples illustrate the present invention and how it relates to similar tires on the market.

EXAMPLE 1

Preferred Method of Sealant Tire Building

Truck Bus Radial (TBR) tire of size 215/17R17.5 was built. First applied sealant cover layer of same width as inner liner was applied to tire building drum, then two layers of low viscosity sealant precursor B and then two layers of higher viscosity sealant precursor 4C014A. The widths of sealant precursor layers were approximately same as tread width. Then full width inner liner was applied followed by other normal layers for tire build. After green tire was built, 2 mm Dartek C917 film was applied on the top of sealant cover layer covering the sealant precursor underneath followed by curing. After cure, Dartek C917 film was removed before testing. When the tire came out from press, there was initial bulging of sealant cover layer which later receded once the tire cooled.

Uniformity Test

FDBRC-6142TD-R from KOKUSAI was used for tire uniformity test. The tire with sealant layer had uniformity A.

Nail Hole Sealant Tests

It was done after inflating the tire to 116 psi. This tire passed nail hole test with 12d and 16d nails but failed with 20d nail. Nails of sizes 12d, 16d and 20d have respective diameters of 0.148, 0.162 and 0.192 inches or 3.8, 4.1 and 4.9 millimeters.

Sealant Thickness Cured Tire

The tire was cut and the sealant thickness was determined to be 4 mm.

EXAMPLE 2

Nail Hole Sealing Capability with Single Layer of Sealants VS Two Layers

215/75R17.5 TBR Tires were built with one layer of sealant and two layers of sealant of equal combined thickness as shown in Table 3.

No. 1A and 1B of Table 3 shows puncture sealing properties of combination of two different sealant layers (4C014A and 4C014B) of total thickness 4.8 mm. Both sealed holes inflicted by 20d nails when applied on tread lug. 1A failed to seal hole inflicted by 20d nail on tread groove while 1B successfully sealed hole inflicted by 20d nail on tread groove. This suggests that lower viscosity sealant is preferred as the layer inner to the higher viscosity sealant. This also suggests that the lower viscosity sealant helps push the higher viscosity sealant into the nail hole thus plugging the nail hole without oozing out of the outer tread surface.

No 1C and 1D of Table 3 has one viscosity sealant (like Goodyear's Duraseal tires and others with reference 1-11) of total thickness 4.8 mm. Both the sealants showed inferior nail hole puncture sealing capability compared to combination of two viscosity sealant layers 1A and 1B of equivalent total thickness.

Table 3

Puncture Testing of 215/75R17.5 TR685 TBR Tire with Sealant Layers

No	Sealant Layer	Nail in Groove			Nail in Lug
		12d	16d	20d	20d
1A	Inner liner 3.2 mm 4C014A (Low Viscosity) 1.6 mm 4C014B (High Viscosity) 4C013B (Cover layer) PRESENT INVENTION	Passed	Passed	Failed	Passed
1B	Inner liner 1.6 mm 4C014B (High Viscosity) 3.2 mm 4C014A (Low Viscosity) 4C013B (Cover layer) PRESENT INVENTION	Passed	Passed	Passed	Passed
1C	Inner liner	Failed	-	-	Failed

	4.8 mm 4C014A (Low Viscosity) 4C013B (Cover layer) PRIOR ART (1-11)				
1D	Inner liner 4.8 mm4C014 B (High Viscosity 4C013B (Cover layer) PRIOR ART (1-11)	Passed	Failed	-	Passed

EXAMPLE 3

Sealant Cover Layers

Identical tires were made by varying the sealant cover layers as shown in Table 4. Table 5 shows that sealant came out from tread when 4C013A sealant cover was used. Sealant did not come out when 90BIIR/10CSM sealant cover layer was used where BIIR is bromobutyl and CSM is chlorosulfonated polyethylene. Composition of 90BIIR/10CSM is similar as composition in Table 1 except that 100 BIIR is replaced with 90BIIR and 10CSM. Cut tire showed that when 90BIIR/10CSM was used, sealant cover layer stretched and plugged the nail hole. This did not occur when 4C013A sealant cover layer was used as the M100 was very high (2.99 MPa) and it takes a lot of force to stretch.

Low M100 sealant cover can also be compounded using conventional rubber without butyl or halobutyl as shown in Tables 7 and 8.

Current commercial Duraseal tires use very thick inner liner which cannot stretch and plug the nail hole.

In the present invention, when a sealant cover layer was used, it has 100% modulus of 1.6 MPa (range 0.5 – 2.5 MPa and preferably 1.2 – 1.9 MPa).

Table 4

Properties of two different sealant cover layer

A3T ID	**4C013A**	**90BIIR/10CSM**
Tensile (MPa)	17.0	9.3
E (%)	446	642
M100 (MPa)	2.99	1.6
M300 (MPa)	8.65	4.3

Table 5

Puncture Testing of 315/80R22.5 Tires with two different sealant cover layer

No	Sealant Layer	Nail hole testing	Comments
2F	14cmX14cm Orange 4C014B 2X(14 cm X 14 cm Green 4C014A 20 cm X 20 cm 4C013A	12d – Passed 16d Passed 20d – Passed	Some sealant came out on surface with 16d and 20d
2G	14cmX14cm Orange 4C014B 2X(14 cm X 14 cm Green 4C014A 20 cm X 20 cm 90BIIR / 10 CSM (GM in-line inner liner)	12d – Passed 16d Passed 20d – Passed	No sealant came out of tread

Table 6

Examination of Inner Liner of 315/80R22.5 Tires after Puncture Test

No	Innermost Layer	Nail	Condition of Innermost layer
2F	4C013A	12d 16d 20d	Inner most layer did not stretch to plug the nail hole
2G	**90BIIR/10CSM**	12d 16d 20d	Inner liner stretched and plugged the nail hole

Table 7

Mixing of two red innermost sealant cover layer

		4C013A	**4C022A**
Ingredient	Stage	Amount (phr)	Amount (phr)
Natural Rubber	NP1	70.00	70.00
SBR-1502	NP1	30.00	30.00
Silane treated clay	NP1	27.5	27.5
Titanium Dioxide	NP1	5	5
Hi-Sil135 (150 BET)	NP1	32.00	-
Ultra-Sil 360 (55 BET)	NP1	-	16
Medium Process Oil	NP1	1.00	1.00
Stearic Acid	NP1	1.5	1.5
Polymeric hindered phenol	NP1	1.5	1.5
Zinc Oxide	NP1	20	20
Red Rubber Concentrate	NP1	1.00	2.00
Total NP1		190.5	189.5
NP1	PR	190.5	189.5
Diphenyl Guanidine	PR	0.20	0.20
Benzothiazyl disulfide (MBTS)	PR	2.00	2.00
Insoluble Sulfur	PR	1.83	0.6
ZBED	PR	0.75	0.75
TBzTD	PR	1.00	1.00
TOTAL		196.28	194.05

Table 8
Properties Red Rubber Compound of Table 7

A3T ID	4C013A	4C022A
ODR at 302°F/R100/18-24'/3°Arc		
Ts2 (min)	3.45	4.56
Tc90 (min)	12.18	11.27
ML	11.42	10.19
MH	80.12	59.38
Δ Torque	68.70	49.19
Cured Property (7 min at 320°F)		
Duro	62	48
Tensile (MPa)	17.0	18.5
E (%)	446	588
M100 (MPa)	2.99	1.5
M200 (MPa)	5.58	2.9
M300 (MPa)	8.65	4.6
Tear, Die C (lbs/inch)	162	155
Estimated Sp. Gravity	1.315	1.281
Green Strength		
Tensile (MPa)	0.40	0.57
% Elongation	942	995
M100 (MPa)	0.35	0.29
M200 (MPa)	0.33	0.28
M300 (MPa)	0.33	0.30
Mooney Viscosity		
ML (1+4) at 212°F	50.05	35.61
Scorch at 250°F		
T5 (min)	25.48	26.24
Minimum Viscosity	39.99	> 26

EXAMPLE 4

RPA Measurements of Sealants

Rubber Process Analyzer (RPA) is widely used in rubber industry. The RPA-2000 model can be purchased from Alpha Technologies. It measures rubber properties before cure, during cure and after cure.

Following was RPA test conditions of 4 sealants and one sealant cover and the results are shown respectively in Tables 9 and 10.

Step #1 - 80°C, 5% strain, 1 Hz and determine storage modulus

Step #2 - heat the sample for 12 minutes at 170°C, 5% strain, 1 Hz

Step #3 - Cool to 80°C and repeat step #1

Step #4 - Cool to 35°C and repeat step #1

Storage modulus (G') can be related to viscosity of material. In Table 9, before heat, G' values are for sealant precursors. After heat, G' are for sealants. Four sealants have G' values at 35°C in the range 0.056 – 0.406 MPa. Same four sealants have G' values at 80°C in the range 0.01 – 0.194 MPa. If 0.3 – 0.41 G' is best for sealing nail hole, then sealant RC4C014 is desired if puncture occurs at 35°C while 4C021B is desired if puncture occurs at 80°C. This data shows that two layers of sealant of different viscosities are preferred over one viscosity sealant as puncture can occur at different temperatures.

Before heat G' of one of the sealant cover layer (Table 10) at 80°C is lower than G' at 80°C of high viscosity sealant layer after heat (0.144 MPa vs 0.194MPa) (Table 9). This shows that high viscosity sealant layer can be formulated without the need of any peroxide or curatives. One example of such high viscosity sealant layer is NP1 of 4C022A without the curatives as shown in Table 7.

Table 9

RPA of the Four Sealant Layers in the Ascending Order of G' at 35°C after Thermal Breakdown

Compound	Before Heat at 80°C		After Heat at 80°C		After Heat at 35°C	
	G' (MPa)	Tan ∂	G' (MPa)	Tan ∂	G' (MPa)	Tan ∂
RC4C014D	0.245	0.302	0.194	0.555	0.406	0.349
RC4C014C	0.237	0.305	0.059	0.891	0.196	0.627
4C021B = 4C014B	0.149	0.334	0.035	1.037	0.134	0.55
4C021A = 4C014A	0.149	0.338	0.010	1.449	0.056	1.072

Table 10

RPA Results of Sealants Cover Layer

Compound	Before Heat at 80°C		After Heat at 80°C		After Heat at 35°C	
	G' (MPa)	Tan ∂	G' (MPa)	Tan ∂	G' (MPa)	Tan ∂
4C022A	0.144	0.493	0.567	0.047	0.511	0.077

EXAMPLE 5

Storage Modulus Range of High and Low Viscosity Sealants

Tables 11 and 12 shows tire tests where different ranges of high and low viscosity sealants were used. G' after heat is related to viscosity of sealant. Eight tests are shown in Tables 11 and 12. For high viscosity sealant, G' is in the range 0.405 MPa – 0.134 and for low viscosity sealant, G' is in the range 0.196 - 0.056 MPa. As the tables show, G' at 35°C of high viscosity sealant is in the range 0.5 – 0.1 MPa. This kind of material can be made without the

need of any peroxide or curative. G' at 35°C of low viscosity sealant is in the range 0.3 – 0.02 MPa. This kind of material can only be generated from precursor with peroxide as otherwise it will be very difficult to process.

Peroxide catalyst is used for degradation of butyl rubber to low molecular weight rubber. The catalyst must be stable at room temperature. The catalyst should also degrade below tire cure temperature i.e. 150°C. In other words, we can use one or more peroxide catalyst that has Self-Accelerated Decomposition Temperature (SADT) in the range 50 – 140°C. Some examples of such catalysts that we can use are as follows:

Peroxide	SADT (°C)
Val 40 from Akrochem n-Butyl-4,4'-di(t-butylperoxy)valerate	75
Luperox 101 from Arkema DDPH-50 from Akrochem Trigonox® 101 from AkzoNobel 2,5-Di(t-butylperoxy)2,5-dimethyl hexane	80
Di-Cup 40KE Dicumyl peroxide	93
Vul-Cup 40KE 1,3- or 1.4-Bis(tert-butylperoxyisopropyl)benzene	70

Sealant precursor compositions are shown in Tables 13 and 14.

Table 11
Sealant and Sealant Cover Layers Inner to Tire Inner Liner in a 315/80R22.5 Tire. The Tire Passed Punctures Inflicted by 20d Nail when inflated to standard 0.83 MPa (120 psi)

		# 1	# 2	# 3	# 4
High Viscosity Sealant Layer	ID	R4C014D	R4C014D	R4C014F	R4C014F
	Thickness	1.5 mm	1.5 mm	1.5 mm	1.5 mm
	G' at 35°C	0.405 MPa	0.405 MPa	-	-
	G' at 80°C	0.194 MPa	0.194 MPa	-	-
Low Viscosity Sealant Layer	ID	R4C014C	R4C014C	R4C014E	R4C014E
	Thickness	3.0 mm	1.5 mm	3.0 mm	3.0 mm
	G' at 35°C	0.196 MPa	0.196 MPa	-	-
	G' at 80°C	0.059 MPa	0.059 MPa	-	-
Sealant Cover	ID	GM	GM	GM	GM
	Thickness	1 mm	1 mm	1 mm	1 mm

Table 12
Sealant and Sealant Cover Layers in a Tire Inner to Tire Inner Liner that Sealed Punctures Inflicted by 20D Nail

		# 5	# 6	# 7	# 8

High Viscosity Sealant Layer	ID	R4C014C	R4C014C	4C014B	4C014B
	Thickness	1.5 mm	1.5 mm	1.5 mm	1.5 mm
	G' at 35°C	0.196 MPa	0.196 MPa	0.134 MPa	0.134 MPa
	G' at 80°C	0.059 MPa	0.059 MPa	0.035 MPa	0.035 MPa
Low Viscosity Sealant Layer	ID	R4C014E	R4C014E	4C014A	4C014A
	Thickness	3.0 mm	1.5 mm	3.0 mm	1.5 mm
	G' at 35°C	-	-	0.056	0.056
	G' at 80°C	-	-	0.010	0.010
Sealant Cover	ID	GM	GM	GM	GM
	Thickness				

Table 13

Compositions of two sealant precursors

First Time Mixed for Weihai		**4C014A**	**4C014B**
Second Time Mixed for RPA		**4C021A**	**4C021B**
	Stage		
Butyl Rubber	NP	100.00	100.00
Bromobutyl		5	0
Polybutadiene		-	5
Paraffinic oil	NP	13.00	13.00
Silica (higher particle size) – Silene 732D	NP	20.00	20.00
Clay	NP	10.00	10.00
Titanium Dioxide	NP	2.0	2.0
Talc	NP	0.5	0.5
Akrosperse E2295 Green	NP	1.0	-
Akrosperse E6615 Orange	NP	-	1.00
HPS11		2	2
NP	PR		
VAL-40C	PR	12	6
TOTAL		**165.5**	**159.5**

Table 14

Compositions of four additional sealant precursors

	R4C014C	R4C014D	R4C014E	R4014F
Butyl 301	100	100	100	100
Bromobutyl	5	-	5	-
Butadiene Rubber (BR900)	-	5	-	5
Paraffinic Oil	13	13	13	13
Silica 175	20	20	20	20
Clay	10	10	10	10
Green color	1	-	1	-
Yellow Color	-	1	-	1
Trigonox 17-40B-gr	12	6	24	14
Total	161	155	173	163

As can be seen, the present invention is an improvement over other tire puncture sealing technologies, such as US Patent No. 8,387,672 to Majumdar. The present invention, by contrast, does not use or require non-woven fiber layer as the "carrier" of the sealant. Instead, pure sealant layers are used without the need of a nonwoven carrier layer.

The foregoing embodiments of the present invention have been presented for the purposes of illustration and description. These descriptions and embodiments are not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above disclosure. The embodiments were chosen and described in order to best explain the principle of the invention and its practical applications to thereby enable others skilled in the art to best utilize the invention in its various embodiments and with various modifications as are suited to the particular use contemplated.

What is claimed is:

1. A tire with a built-in puncture sealant comprising:

a supporting tire carcass comprised of one or more layers of ply, an outer circumferential tread, and a radially inner layer,

a pair of beads,

sidewalls extending radially inward from the axial outer edges of the tread portion to join the respective beads,

a sealant comprising an outer layer of sealant and an inner layer of sealant, disposed inwardly from said tire carcass inner layer,

wherein the outer layer of sealant and the inner layer of sealant have different viscosities, and

wherein said sealant provides self-sealing properties to the tire.

2. Tire of claim 1 wherein said outer layer of sealant has a higher viscosity than said inner layer of sealant, and said inner layer of sealant has a lower viscosity than said outer layer of sealant.

3. A tire with built-in sealant layer comprising:

a supporting tire carcass having an outer circumferential rubber tread and an inner layer,

an optional rubber inner liner disposed inwardly from the inner layer of the supporting carcass, and

a plurality of built-in sealant layers having different viscosities disposed inwardly from the supporting carcass and, if the optional rubber inner liner is present, inwardly from the optional rubber inner liner, an innermost rubber inner liner disposed inwardly from the built-in sealant layer and having a plurality of spaced apart openings extending therethrough with each opening defining an open width.

4. Tire of claim 3 wherein said plurality of built-in sealant layers having different viscosities comprise a lower viscosity sealant and a higher viscosity sealant, wherein said lower viscosity sealant is disposed inwardly from said higher viscosity sealant.

5. The tire of claim 1, further comprising an inner liner affixed to said tire carcass inner layer, and a cover layer, wherein the outer layer of sealant and the inner layer of sealant are disposed between said inner liner and said cover layer.

6. The tire of claim 5, further comprising a gas permeable layer disposed between said sealant and the inner liner to cover any openings.

7. The tire of claim 5, wherein said cover layer has a 100% modulus of 0.5 MPa to 2.5 MPa.

8. The tire of claim 5, wherein said cover layer has a 100% modulus of 1.2 MPa to 1.9 MPa.

9. The tire of claim 2, wherein the higher viscosity sealant has a G' at 35°C in the range 0.5 MPa to 0.1 MPa and is made without the need of any peroxide or curative.

10. The tire of claim 2, wherein the higher viscosity sealant has a G' at 35°C in the range 0.5 MPa to 0.1 MPa and is made using a peroxide or curative.

11. The tire of claim 2, wherein the lower viscosity sealant has a G' at 35°C in the range 0.3 MPa to 0.02 MPa and is generated from a precursor with peroxide.

12. The tire of claim 2, wherein the lower viscosity sealant predominant composition is selected from the group consisting of butyl rubber, brominated isobutylene-isoprene copolymer, and combinations thereof, and having a Mooney viscosity (ML(1+8) 125°C) in the range 5 – 25 MU.

13. The tire of claim 2, wherein the higher viscosity sealant predominant composition is selected from the group consisting of butyl rubber, brominated isobutylene-isoprene copolymer, and combinations thereof, having a Mooney viscosity (ML(1+8) 125°C) greater than the lower viscosity layer and is in the range 25 – 60 MU.

14. The tire of claim 8, wherein said higher viscosity sealant layer is directly formulated using elastomers selected from the group consisting of butadiene rubber, natural rubber, styrene-butadiene rubber, and blends thereof.

15. The tire of claim 1 wherein said two or more layers of sealants are generated using a peroxide having a SADT in the range 50 – 140 °C.

16. The tire of claim 1, wherein said sealant comprises degraded butyl rubber.

17. The tire of claim 1 wherein said sealant is split into two or more parallel circumferential bands.

18. The tire of claim 17 wherein said two or more parallel circumferential bands comprise four bands.

19. A method for making a tire comprising

forming a green tire;

adding a sealant precursor having one or more sealant precursor layers and one or more peroxides to said green tire;

curing said green tire;

wherein said one or more sealant precursor layers degrade during cure to form sealant layers predominantly containing butyl rubber.

20. The method of claim 18, wherein the sealant precursor layers have a Mooney viscosity (ML(1+8) 125°C) in the range 30 – 60 MU.

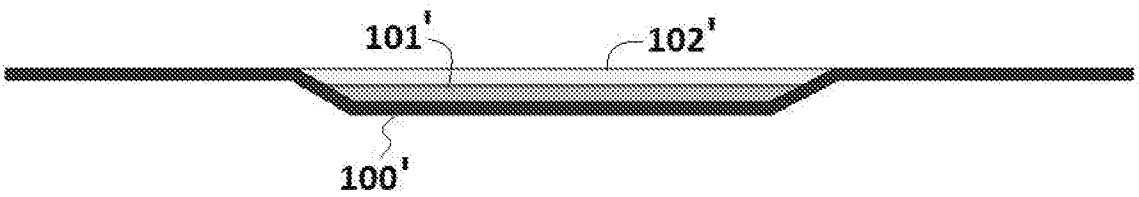


Fig. 1

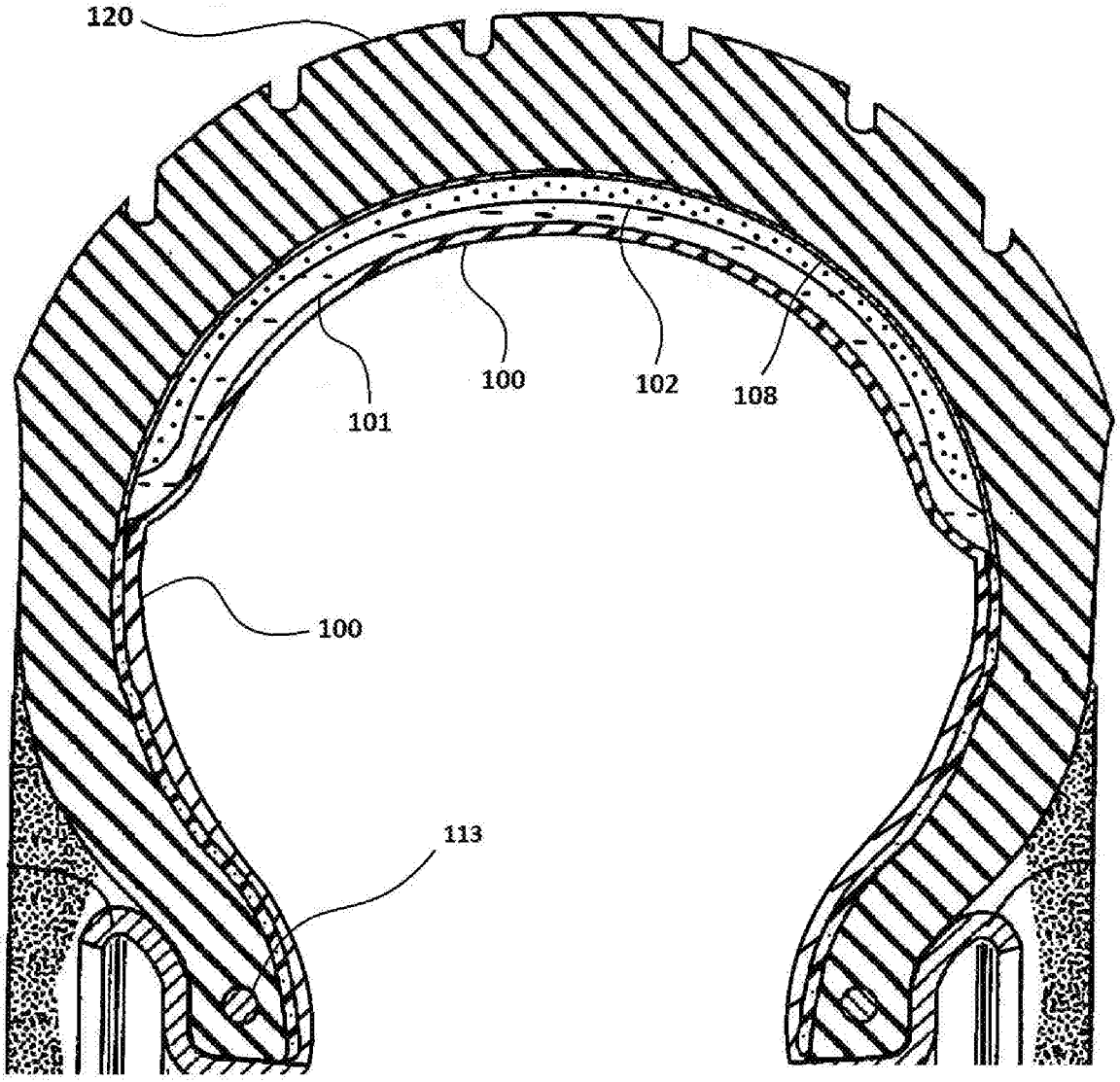


Fig. 2

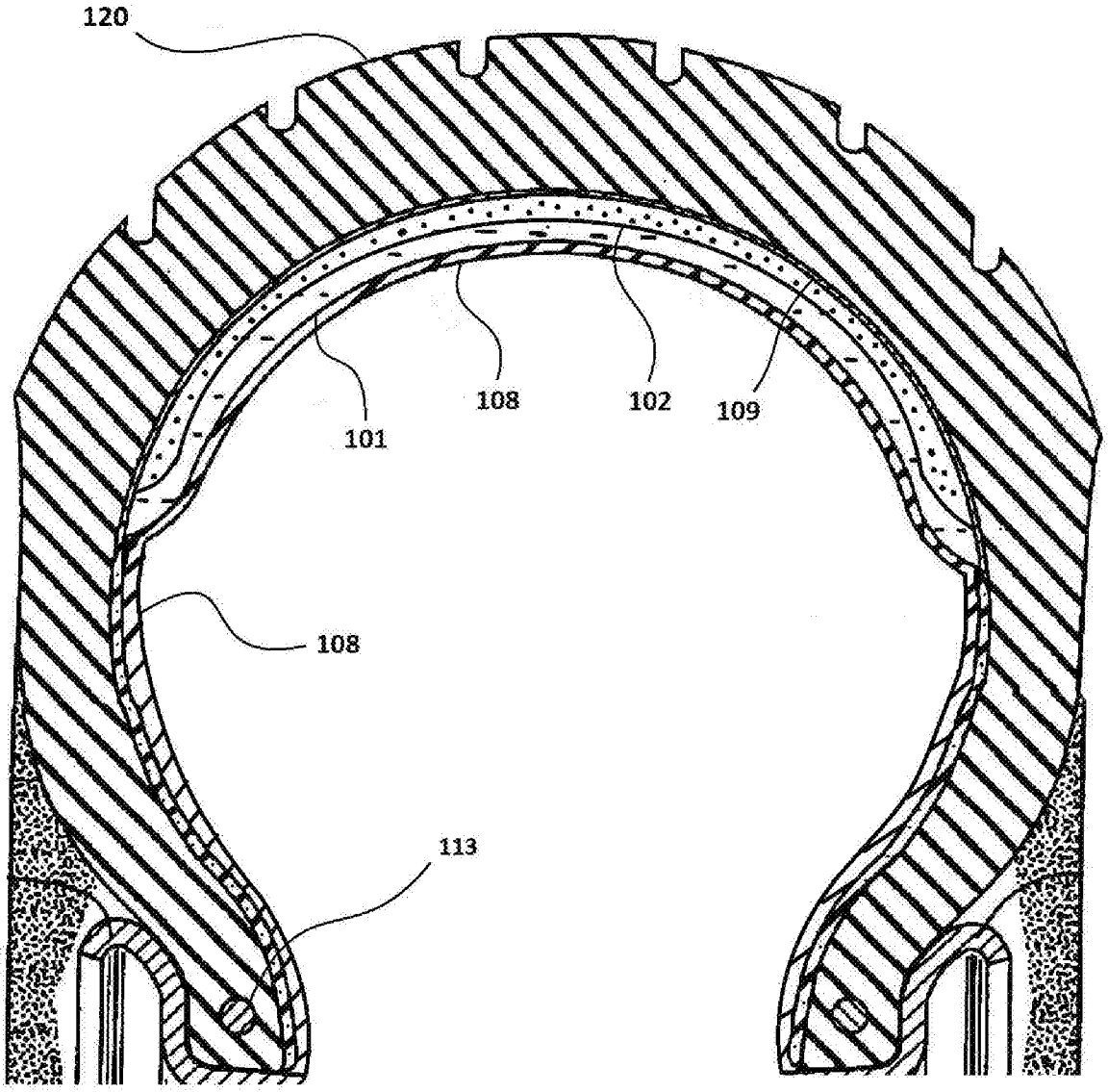


Fig. 3

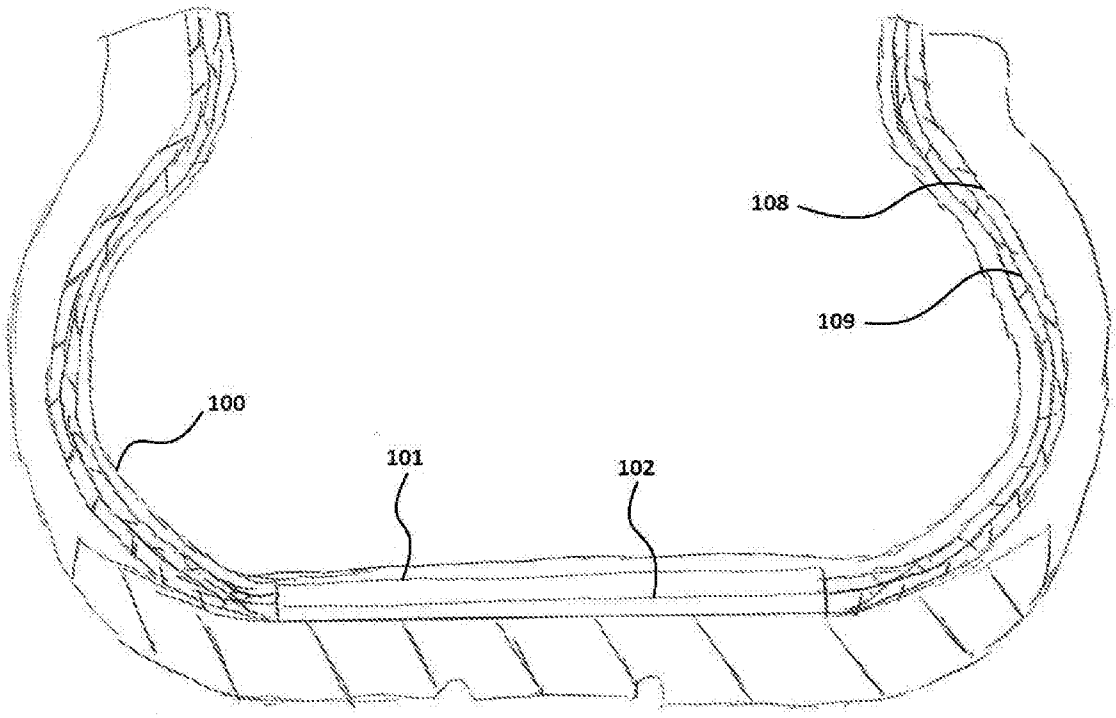


Fig. 4

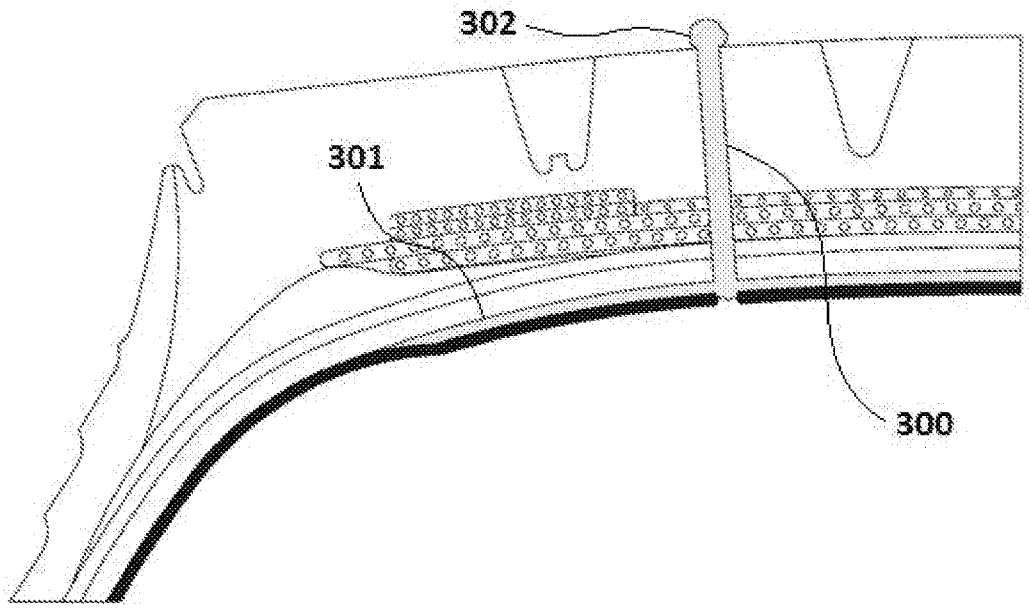


Fig. 5

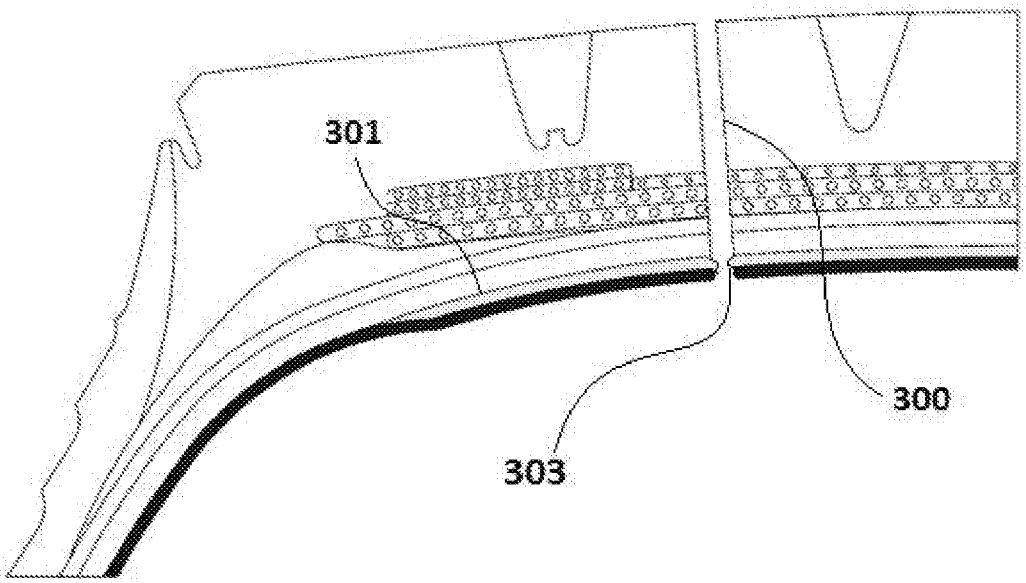


Fig. 5A

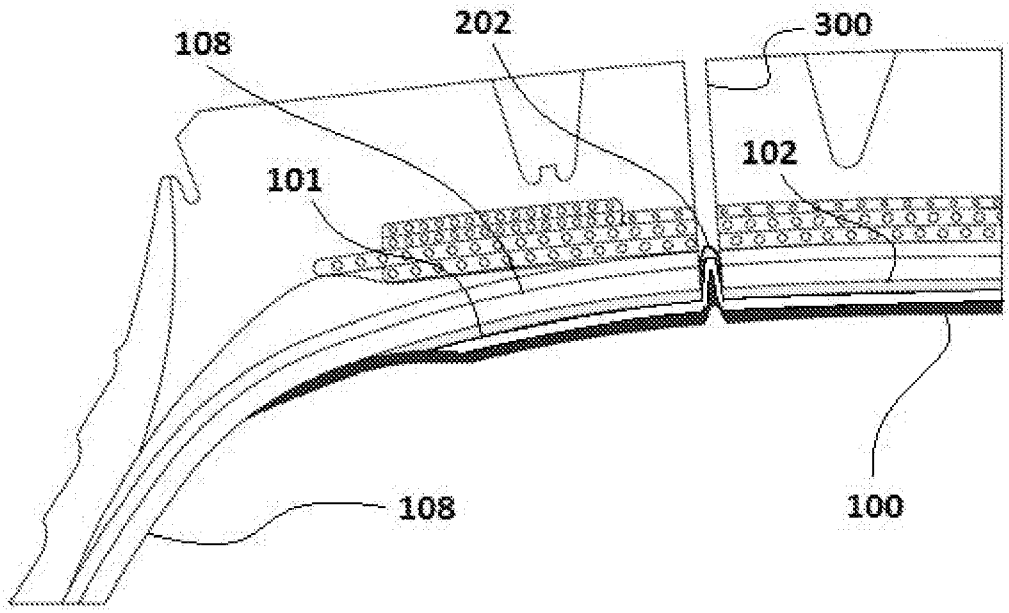


Fig. 6

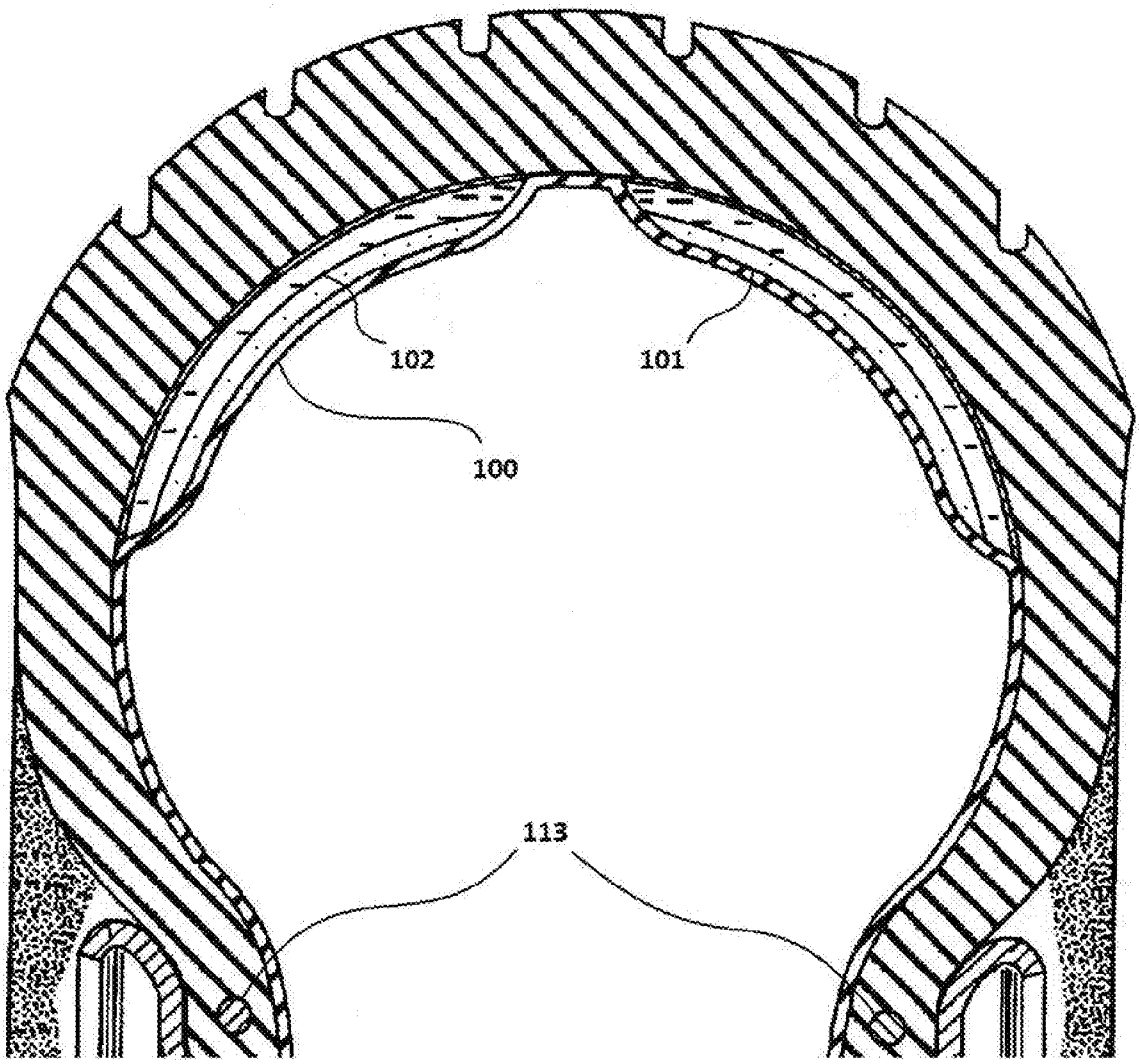


Fig. 7

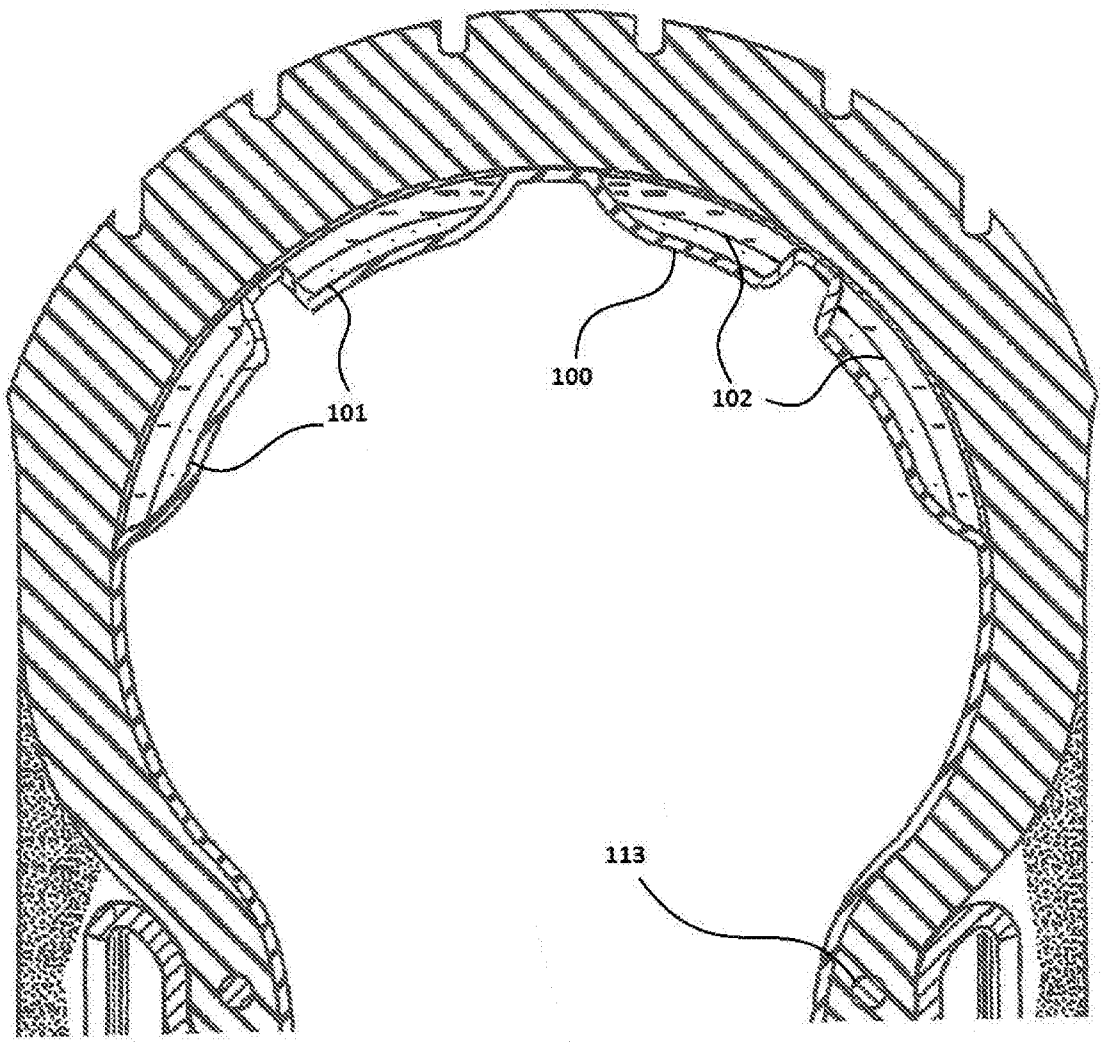


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/086915

A. CLASSIFICATION OF SUBJECT MATTER

B29C 73/22(2006.01)i; B60C 19/12(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B29C73/16; B29C73/18; B29C73/20; B29C73/22; B60C19/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,WPI,EPODOC,tire,tyre,seal+,viscos+,viscidity,opening,width,peroxide ?,cur+,butyl

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011126953 A1 (INCAVO, JOSEPH ALAN) 02 June 2011 (2011-06-02) claim 7, and paragraph 103	19-20
A	US 4665963 A (TIMAR, JOHN ET AL.) 19 May 1987 (1987-05-19) description, column 3, line 63 to column 7, line 62, figures 1 and 4	1-20
A	CN 101535066 A (YOKOHAMA RUBBER CO., LTD.) 16 September 2009 (2009-09-16) the whole document	1-20
A	JP H045030 A (BRIDGESTONE CORP.) 09 January 1992 (1992-01-09) the whole document	1-20
A	JP 2005001547 A (BRIDGESTONE CORP.) 06 January 2005 (2005-01-06) the whole document	1-20
A	CN 1927608 A (YOKOHAMA RUBBER CO., LTD. ET AL.) 14 March 2007 (2007-03-14) the whole document	1-20

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 October 2015	**12 November 2015**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**	**LIN,Xiuxia**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62414227**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/086915

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

[1] The prior art has been identified as document US4665963A, the following technical feature of claim 1 makes a contribution over the prior art and can be considered as a special technical feature within the meaning of Rule 13.2 PCT: the outer layer of sealant and the inner layer of sealant have different viscosities. Claim 3 has the special technical feature also, but the groups of claims 19–20 have not said special technical feature, so it defines claims 19-20 different inventions which are not linked by a single general inventive concept with claim 1. The application, hence does not meet the requirements of unity of invention as defined in Rules 13.1 and 13.2 PCT.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☑ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/086915

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2011126953	A1	02 June 2011	CN	102086289	A	08 June 2011
				EP	2329940	A1	08 June 2011
				BR	PI1009949	A2	25 September 2012
				KR	20110063354	A	10 June 2011
US	4665963	A	19 May 1987	EP	0264506	A1	27 April 1988
				DE	3607089	D1	07 June 1990
				EP	0127998	A2	12 December 1984
				JP	S608103	A	17 January 1985
				KR	910009230	B	07 November 1991
				AU	2874784	A	06 December 1984
				MX	166726	B	29 January 1993
				CA	1217122	A1	27 January 1987
				ES	8506505	A1	16 November 1985
CN	101535066	A	16 September 2009	US	2010071821	A1	25 March 2010
				EP	2082902	A1	29 July 2009
				JP	2008126727	A	05 June 2008
				WO	2008059635	A1	22 May 2008
JP	H045030	A	09 January 1992	None			
JP	2005001547	A	06 January 2005	None			
CN	1927608	A	14 March 2007	JP	2003080909	A	19 March 2003
				JP	2003183623	A	03 July 2003
				US	2008078489	A1	03 April 2008
				CA	245984	C	25 October 2011
				US	2004194862	A1	07 October 2004
				EP	1714802	A1	25 October 2006
				DE	60229798	D1	18 December 2008
				EP	1435301	A1	07 July 2004
				CN	1553866	A	08 December 2004
				JP	2003104007	A	09 April 2003
				JP	2003118330	A	23 April 2003
				EP	1724126	A2	22 November 2006
				KR	20080098453	A	07 November 2008
				WO	03026906	A1	03 April 2003
				JP	2003159917	A	03 June 2003
				KR	20040044476	A	28 May 2004
				KR	20080068144	A	22 July 2008
				DE	60225460	D1	17 April 2008
				DE	60229991	D1	02 January 2009