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(54) Title: A CARBOXYLATED ACRYLONITRILE BUTADIENE LATEX SEAMLESS BLADDER HAVING IMPROVED ADHESION FOR VALVE BODY AND A PROCESS FOR MANUFACTURING THEREOF

(57) Abstract: The present invention relates to a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body, and wherein the bladder comprises bladder body made from carboxylated acrylonitrile butadiene latex provided with at least one coating of a material selected from the group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex. In one embodiment, it also relates to process of preparation thereof. In another embodiment, it also relates to an inflatable ball made therefrom.

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Title of the Invention:-

A Carboxylated Acrylonitrile Butadiene Latex Seamless Bladder having Improved Adhesion for Valve Body and a Process for Manufacturing Thereof.

Field of the Invention:-

The present invention relates to a carboxylated acrylonitrile butadiene latex seamless bladder having improved adhesion for valve body and a process for manufacturing thereof.

Particularly, it relates to a carboxylated acrylonitrile butadiene latex seamless bladder having improved capability to bond with valve body of natural rubber and a process for manufacturing thereof.

Background of the Invention:-

A bladder is an independently saleable commodity. If it is employed in medical applications for gas transfusion etc., it can be employed without any outer cover thereon. However, if it is employed in sport industry for manufacture of balls, particularly for inflatable balls, then it is covered with an outer cover to protect it from bursting and to form a ball. The outer cover is either hand stitched or machine stitched depending upon the game in which it is being used or the desired characteristics and quality of the end product. The hand stitched outer cover is required, for example, in match and practice balls, and machine stitched cover is required, for example, in match and practice balls including promotional balls wherein the volume of demand is relatively higher. The term promotional balls means the balls used by manufacturers and/or promoters to promote their products and events, such as during trade fairs, national games, international games, etc. The physical characteristics of bladder for both types of outer covers are different.

The present invention particularly relates to a carboxylated acrylonitrile butadiene latex seamless bladder having improved capability to bond with valve body of natural rubber, which is particularly suitable for hand stitched inflatable balls. However, it may be understood that the scope of present invention is not restricted by use of disclosed seamless bladder for hand stitched inflatable balls, because surprisingly the present bladder being suitable for hand stitched inflatable balls has also been found suitable for machine stitched balls including, but not limited to inflatable balls, and also for medical applications including gas transfusion.

For inflatable balls, the film for manufacturing a bladder is not only required to be of suitable weight, but is also required to have controlled inflation capability when

inflated as a bladder, to give required shape and size of the ball and to protect the bladder made from such film as well as the outer cover from de-shaping and bursting on inflation.

On the contrary, for medical applications, such as for manufacturing hand gloves, the film for manufacturing the gloves is neither required to be of a suitable weight nor required to have controlled inflation capability as it is neither required to have bounce characteristics nor to be inflated as a bladder to have a particular shape and size, nor is required to be protected from de-shaping and bursting on inflation.

It has been observed that for manufacturing a hand glove, even a very lighter film having weight varying from about 100 to about 200 mg/inch^2 is sufficient because, as stated, it is neither required to have any bounce characteristics nor to have a shape as in case of a ball. Further, the glove is not required to be stitched to any outer cover.

On the contrary, it has been observed that for hand stitched inflatable balls, the film for manufacturing a bladder is required to have relatively very heavy weight varying from about 500 to about 700 mg/inch^2, which has been found suitable for providing the shape and bounce characteristics to the hand stitched balls, because the outer cover of the ball and its stitches are strong enough.

Similarly, for machine stitched inflatable balls, it has been observed that the film for manufacturing a bladder is required to have even further heavier weight varying from about 700 mg/inch^2 to about 1.5 g/inch^2, which has been found suitable for providing the shape and bounce characteristics to the machine stitched balls, because the outer cover of such balls and its stitches are not strong enough as compared to hand stitched balls.

Therefore, a film used for manufacturing a hand glove cannot be employed for manufacturing a bladder suitable for a ball.

It has been further observed that in conventional balls, if bladder is not made of a film having a required weight and controlled inflation capability, the required weight and controlled inflation capability is, then, generally achieved by applying one or more layers of thread breading around the outer layer of the bladder, which has been found to result in increase in the hardness of the bladder, and hence, the bladder does not remain suitable for playing football, and additionally it looses its spherical shape.

In conventionally available inflatable balls, the bladder made from butyl rubber is used. However, such bladders are not of required weight. In case of butyl rubber bladders, the required weight is achieved by increasing its wall thickness which is

determined based on the weight required by employing molding process which is conventionally carried out on an unsupported film made by pasting four panels and not on a bladder *per se*.

The major problem of manufacturing a butyl rubber bladder having required weight by increasing its wall thickness by molding is that the cost of material increases manifold.

Further, the major problem of the molding process is that it cannot be employed if a seamless bladder is required. As present invention aims at providing a seamless bladder, the molding process, therefore, is not suitable.

Still further problem of molding process is that even the joints are not of uniform weight, that is, weight at the joints of the bladder is relatively higher adversely resulting in wobbling effect during flight of the ball.

Yet another problem of molding process is that it has been found to be more expensive, and yet resulting in higher rejection, and hence, effectively lower production rate with higher capital cost.

Further, it has been observed that even by manufacturing the butyl rubber bladder by molding process, the required weight cannot be achieved. Therefore, in case of conventionally available bladders thread breading of nylon fiber around butyl bladder is applied to achieve the desired weight characteristics, which has been found to enhance controlled inflation capability of the bladder produced, but as stated herein, the thread breading results in increase in the hardness of the bladder, and hence, makes it unsuitable for playing football, and additionally loss of its spherical shape.

In US Patent No. 4,191,375, issued on March 4, 1980, a game ball having an inner bladder provided with a layer of yarn fiber is discussed.

The US Patent No. 4,830,373, issued to Dehnert et al, describes a soccer ball which includes an inflatable floating bladder comprising two ply of butyl within a thread form of carcass.

The US Patent Nos. 5,772,545 and 6,390,941 B1 issued to Ou describe use of strengthened nylon thread overlapping each other to form a web like layer which permanently embraces and adheres to the bladder and supports the outer cover of the ball.

The US Patent No. 6,793,597 describes machine stitched ball with floating bladder. It consists of bladder and the outer cover wherein the outer cover is vulcanized

with web of thread and adhesive. Further, the outer surface of the bladder is coated with the silicone releasing chemical before winding.

However, it has been observed that the fiber is applied around outer layer of the bladder in the form of a web like structure which does not allow bladder to inflate more than it has initially inflated for the purpose of breading by nylon fiber. Therefore, such bladders suffer from problem of limited inflation.

Further, as stated herein, it has been observed that due to thread breading, the bladder becomes harder, which limits its applications and wide acceptability because harder is the bladder, the players are hit harder during playing, for example, while kicking, heading etc. This problem can be overcome, but by providing additional padding between thread breading of the bladder and outer cover of the ball, which in-turn adds on the cost of the end product – ball, and hence make it commercially unviable.

Further, when a bladder is used in sports industry, it is desired that it should have judicious combination of bounce as well as air retention characteristics without sacrificing one property for the another property.

It has been observed that bladders made from synthetic butyl rubber exhibit good air retention characteristics, but have poor bounce characteristics. Such bladders have been accepted, but the need for seamless bladder having judicious combination of good air retention characteristics and good bounce characteristics, and still having low manufacturing cost, high productivity and low rejection rate has not been satisfied.

Further, the bladders made from natural rubber exhibit good bounce characteristics, but have poor air retention characteristics. Such bladders have also been accepted, but the need for seamless bladder having judicious combination of good air retention characteristics and good bounce characteristics, and still having low manufacturing cost, high productivity and low rejection rate has not been satisfied.

It has been observed that even the bladders made from conventionally used synthetic latex exhibit good air retention characteristics, but have poor bounce characteristics.

Further, it has been observed by the inventors of the present invention that when a bladder is made from synthetic latex, particularly from synthetic acrylonitrile butadiene latex, the processability of the synthetic latex to have a film of desired thickness and weight is not possible.

It has been found that bladders made from synthetic acrylonitrile butadiene latex film are of thickness varying upto about 0.20 mm. The main drawback of a film of synthetic acrylonitrile butadiene latex having such a lower thickness is that stripping of film becomes very difficult.

Further, the inventors of the present invention have found that if a film of synthetic acrylonitrile butadiene latex for manufacture of a bladder having thickness more than about 0.25 mm is achieved, then drying problem is observed during manufacture of a film which in-turn has been found to cause cracks in the film.

It has been further found that bladders made from synthetic acrylonitrile butadiene latex film are of weight varying upto about 300 mg/inch^2, which as described herein, have not been found suitable for providing the shape and bounce characteristics even of the hand stitched balls, because as described herein, a film to manufacture a bladder suitable for hand stitched inflatable balls should have relatively very heavy weight varying from about 500 to about 700 mg/inch^2 and for machine stitched inflatable balls should have even further heavier weight varying from about 700 mg/inch^2 to about 1.5 g/inch^2.

Still another problem observed with synthetic acrylonitrile butadiene latex is that it results in a film having modulus varying from about 10 to 12 Kg/Cm^2 at 100% stretch [or elongation], which has been found to be a main cause of resulting in a bladder having poor bounce characteristics.

Yet another problem observed with synthetic acrylonitrile butadiene latex is that it results in a film having poor cross-linking as found by measuring tensile strength which has been found to be varying from 60 to 70 kg/cm^2 and elongation at break which has been found to be varying from 450 to 500%. Such a poor cross-linking has been found to be another cause of resulting in a bladder having poor bounce characteristics as well as reduced air retention characteristics.

Even further it has been observed that bladder made from film of synthetic acrylonitrile butadiene latex gets tear-off from its neck during stripping from a mould resulting in total loss of production.

Further, such bladders made from conventionally used synthetic latex do not have required bounce and controlled inflation characteristics. Therefore, such bladders have not been commercially acceptable.

Therefore, it can be concluded that the conventionally used synthetic latex, particularly the synthetic acrylonitrile butadiene latex is not suitable for manufacturing a film suitable for manufacturing a bladder for inflatable balls.

Further, the bladders made from natural latex exhibit good bounce characteristics, but have poor air retention characteristics. Such bladders have been accepted, but the need for a bladder having judicious combination of good air retention characteristics and good bounce characteristics, and still having low manufacturing cost, high productivity and low rejection rate has not been satisfied.

Accordingly, it has been found that when conventionally available bladders are made either from conventionally used synthetic rubber or synthetic latex, or from conventionally used natural rubber or natural latex, these have either poor air retention characteristics or poor bounce characteristics. Therefore, neither the bladders made from conventionally used synthetic rubber or synthetic latex, nor the bladders made from conventionally used natural rubber or natural latex have been commercially acceptable.

Therefore, a need to have a bladder having judicious combination of bounce characteristics as well as air retention characteristics, and controlled inflation capability without sacrificing one property for the another property has been felt for an inflatable ball.

An attempt has been made to manufacture bladders by employing blends of natural rubber and synthetic rubber.

However, it has been found that even bladders made from blends of natural rubber and synthetic rubber suffer primarily from poor curing, i.e. cross linking, which in-turn results in low bounce characteristics. Even blends of synthetic rubber with natural rubber have not been able to result in a bladder having good bounce as well as good air retention characteristics.

Another problem of bladders made from blends of natural rubber and synthetic rubber is that these are not seamless as these are made by employing molding process, and hence, do not have uniform weight over the entire area, which in-turn results in an inflatable ball having wobbling effects, and therefore, higher rejection rate of the bladders and balls made therefrom.

Still another attempt has been made to manufacture bladders by employing blends of natural latex and synthetic latex, wherein such bladders are manufactured by employing dipping process, and wherein synthetic latex is selected from a group

consisting of synthetic acrylonitrile butadiene latex, neoprene [for example polychloroprene latex], isoprene [for example, polyisoprene latex], SBR [styrene butadiene rubber] and natural latex is commonly known as centrifuged latex.

However, it has been found that even bladders made from blends of natural latex and synthetic latex suffer primarily from poor curing, i.e. cross linking, which in-turn results in low bounce characteristics. Even blends of synthetic latex with natural latex have not been able to result in a bladder having good bounce as well as good air retention characteristics.

Accordingly, it has been found that when conventionally available bladders are made either from blends of natural rubber and synthetic rubber or from blends of natural latex and synthetic latex, these have poor curing, and hence, have poor bounce characteristics, and in-addition bladders made from blends of natural rubber and synthetic rubber are not seamless bladders. Therefore, neither the bladders made from natural rubber and synthetic rubber nor the bladders made from natural latex and synthetic latex have not been acceptable, because these bladders also lack judicious combination of good air retention characteristics and good bounce characteristics.

Yet another attempt has been made to manufacture bladders by employing laminates of natural latex and synthetic latex, wherein synthetic latex is selected from a group consisting of synthetic acrylonitrile butadiene latex, neoprene [for example polychloroprene latex], isoprene [for example, polyisoprene latex], SBR [styrene butadiene rubber] and natural latex is commonly known as centrifuged latex.

However, it has been found that even bladders made from laminates of natural latex and synthetic latex primarily suffer not only from poor curing, i.e. cross linking, which in-turn results in low bounce characteristics, but also from problem of delamination of layers of the laminate, which in-turn results in bursting during performance, and hence, further rejection of the bladder. Accordingly, even laminates of natural latex and synthetic latex have not been able to result in a bladder having good bounce as well as good air retention characteristics, and good strength of the laminate *per se* to result in strong enough bladder.

Therefore, it has been found that even the bladders made from laminates of natural latex and synthetic latex have not been commercially acceptable.

Even another attempt to manufacture bladders by employing laminates of natural rubber and synthetic rubber has not been commercially successful.

It has been found that even bladders made from laminates of natural rubber and synthetic rubber primarily suffer not only from poor curing, i.e. cross linking, which in-turn results in low bounce characteristics, but also from problem of delamination of layers of the laminate, which in-turn results in bursting during performance, and further rejection of the bladder. Accordingly, even laminates of natural rubber and synthetic rubber have not been able to result in a bladder having good bounce as well as good air retention characteristics, and good strength of the laminate *per se* to result in strong enough bladder.

To overcome above discussed problems of prior art, the PCT Patent Application No. PCT/IN2008/000085 [PCT'85] discloses a seamless bladder having combination of good air retention characteristics as well as good bounce characteristics for inflatable balls, wherein the bladder is made from carboxylated acrylonitrile butadiene latex and no other latex.

The inventors, during industrial production of bladder of PCT'85 have found that the bonding of bladder with valve body essentially requires coating of a primer and neoprene rubber [NR] adhesive to both the surfaces, i.e. surface of bladder made from carboxylated acrylonitrile butadiene latex and no other latex, and of valve body made from natural rubber, and such coating process requires following repeated steps of:-

i) coating a primer onto surface of bladder;

ii) coating neoprene rubber [NR] adhesive onto coated surface of bladder from step i);

iii) drying the coated surface of bladder from step ii) at about 40-45^{0}C with heat blower;

iv) repeating steps of coating i) and ii) onto dried coated surface of bladder from step iii);

v) drying the coated surface of bladder from step iv) at about 40-45^{0}C with heat blower;

vi) performing steps i) to v) onto surface of valve body;

vii) fixing valve body from step vi) onto bladder from step v).

The above steps of coating not only add to time of production, but also add to cost of production, and therefore, makes the overall process highly uneconomical on industrial scale.

Further, the above coating process steps can only be performed on surfaces of bladder and valve body after performing step of buffing. The inventors have found that step of buffing results in problems and risk of tearing of bladder, and hence, in rejection of bladders, which results in additional loss of production, and therefore, makes the overall process further highly uneconomical on industrial scale.

Need of the Invention:-

Therefore, there is still a need to have a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body and a process for manufacturing thereof, which overcome above-described problems of prior art, including problems of bladder of PCT'85, and wherein the production cost is substantially reduced by reducing process time, process cost and rejection rate, and by increasing the productivity, and the bladder is still suitable for hand stitched as well as machine stitched inflatable balls, and has judicious combination of good air retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

Objects of the Invention:-

Accordingly, the main object of the present invention is to provide a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body and a process for manufacturing thereof, which overcome above-described problems of bladder of PCT'85, and wherein the production cost is substantially reduced by reducing process time, process cost and rejection rate, and by increasing the productivity, and the bladder is still suitable for hand stitched as well as machine stitched inflatable balls, and has judicious combination of good air retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

This is also an object of the present invention to provide a seamless bladder which overcomes one or more above-described problems of the prior art.

Another object of the present invention is to provide a seamless bladder, which is capable of protecting its outer cover from bursting whether it is hand stitched or machine stitched, and hence, has wider acceptability and applicability.

Still another object of the present invention is to provide a seamless bladder, which not only has required and suitable weight, but also has required controlled

inflation, and hence, is capable of giving required shape and size of the ball and protecting the outer cover from de-shaping and bursting on inflation.

Yet another object of the present invention is to provide a seamless bladder, wherein it is manufactured by a process which is capable of resulting in a seamless bladder having no joints, and hence, having uniform weight, and therefore, having no wobbling effect during flight of the ball, and still with no substantial increase in cost of material and process *per se*, and still having increased production rate with substantially reduced capital cost and rejection rate.

This is also an object of the present invention to provide a seamless bladder, which does not get tear-off from its neck during stripping from a mould, and hence, does not result in loss of production.

This is also an object of the present invention to provide a seamless bladder, which does not suffer from problem of delamination of layers, and therefore, no problem of bursting during performance and further rejection thereof.

Other objects and advantages of the present invention will become more apparent from the following description when read in conjunction with the accompanying examples which are not intended to limit scope of the present invention. It may be noted that the accompanying examples are only for the illustration purpose.

Description of the Invention:-

With aim to overcome above-described problems of prior art, particularly of bladder of PCT'85, the inventors have found that if a coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex is applied onto the bladder made from carboxylated acrylonitrile butadiene latex and no other latex, it, surprisingly and unexpectedly, not only overcomes above-described problems of bladder of PCT'85 by avoiding requirement of repeated steps of coating of primer and special neoprene rubber adhesive onto the bladder, and repeated steps of heating to drying the said coatings on the bladder, but at the same time, it also results in substantial reduction in production cost by reducing process time, process cost and rejection rate, and by increasing the productivity.

The inventors have also found that the bladder made from carboxylated acrylonitrile butadiene latex having a coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex is still suitable for hand stitched as well as machine stitched inflatable balls, and has been found to have judicious combination of good air

retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

The inventors have also found that the bladder made from carboxylated acrylonitrile butadiene latex having a coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex, surprisingly and unexpectedly, bonds or adheres to the valve body provided only with a coating of natural rubber based adhesive, and without requiring repeated steps of coating of primer and special neoprene rubber adhesive, and repeated steps of heating thereof to dry the coatings, and therefore, overcomes above-described problems of industrial production of inflatable football from bladder of PCT'85.

The inventors have also found that the football made from the bladder of carboxylated acrylonitrile butadiene latex having a coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex provided with valve body has been found to have judicious combination of good air retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

Accordingly, the present invention relates to

a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body,

wherein the bladder comprises

a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex,

wherein said bladder body is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex.

The seamless bladder of present invention has been found to be suitable for hand stitched and machine stitched inflatable balls.

The seamless bladder body of present invention is additionally provided with a valve body.

In accordance with one of the preferred embodiments of the present invention, the coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex on the bladder body is of thickness varying from about 0.02 mm to about 0.20 mm, preferably the coating is of thickness varying from about 0.03 mm to about 0.15 mm.

Accordingly, the present invention also relates to a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body, wherein the bladder comprises a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, which is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, wherein the bladder has judicious combination of good air retention characteristics and good bounce characteristics without sacrificing one property for the another property, and is used for hand stitched and machine stitched inflatable balls.

In one embodiment, the present invention relates to

a hand stitched or machine stitched inflatable ball made from seamless bladder,

wherein the seamless bladder comprises a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, and

the bladder body is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex.

In another embodiment, the present invention relates to

a hand stitched or machine stitched inflatable ball made from seamless bladder,

wherein the seamless bladder comprises a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, and

the bladder body is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, and

the seamless bladder body is provided with a valve body.

In accordance with present invention, the valve body is adhered or bonded to said seamless bladder body with at least one coating of natural rubber based adhesive.

Accordingly, the present invention also relates to

a ball comprising:

a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body,

wherein the seamless bladder comprises

a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, and

the bladder body is provided with at least one coating of a material selected from group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, and

wherein the seamless bladder body is provided with a valve body,

wherein the valve body is provided with at least one coating consisting of natural rubber based adhesive, and

wherein the valve body is adhered or bonded with (or to) the bladder body.

The seamless bladder of present invention has been found to have judicious combination of good air retention characteristics and good bounce characteristics without sacrificing one property for the another property, and has been found suitable for hand stitched and machine stitched inflatable balls.

Accordingly, the advantages of present invention include avoiding repeated coatings of primer and neoprene rubber adhesive onto the bladder body before adhering or bonding the valve body thereon.

The seamless bladder provided with valve body of present invention has been found to be suitable for hand stitched and machine stitched inflatable balls, and found to have judicious combination of good air retention characteristics and good bounce characteristics without sacrificing one property for the another property.

Accordingly, the present invention also relates to hand stitched and machine stitched inflatable ball comprising:

i) seamless bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, wherein said bladder body consisting of carboxylated acrylonitrile butadiene latex is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, and

ii) valve body adhered or bonded to said seamless bladder body, wherein the valve body is adhered or bonded to the bladder body with at least one coating consisting of natural rubber based adhesive.

In accordance with one of the preferred embodiments of the present invention, the coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex on the bladder body of the ball of present invention is of thickness varying from about 0.02 mm to about 0.20 mm, preferably the coating is of thickness varying from about 0.03 mm to about 0.15 mm.

In accordance with one of the preferred embodiments of the present invention, the coating consisting of natural rubber based adhesive on the valve body of the ball of present invention is of thickness varying from about 0.005 mm to about 0.03 mm, preferably the coating is of thickness varying from about 0.01 mm to about 0.015 mm.

Accordingly, the advantages of present invention include avoiding repeated coatings of primer and neoprene rubber adhesive onto the bladder body before adhering or bonding the valve body thereon, and fitting the bladder body with valve body into the hand stitched and machine stitched inflatable ball body covering.

Accordingly, in one embodiment, the present invention also relates to a process for manufacture of a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body, wherein the process comprises steps of:

A) cleaning the multiple moulds by rinsing in an acid bath;

B) heating the rinsed formers obtained from process step – A) by dipping in hot water;

C) dipping the heated moulds from process step – B) in a coagulant bath;

D) drying the coagulant coated formers obtained from process step – C);

E) dipping the dried and coagulant coated formers obtained in process step – D) in compounded latex bath of carboxylated acrylonitrile butadiene latex [CABL];

F) drying the latex coated coagulated films obtained from process step – E);

G) beading the substantially dried latex coated coagulated films obtained from process step– F) to form a bead followed by leaching;

H) drying and vulcanizing the leached formers with bladder obtained from process step – G);

I) cooling and washing the vulcanized bladders obtained from process step – H); and

J) stripping the cooled and washed bladders obtained from process step – I) from the respective moulds [formers];

characterized in that

the process step - G) is performed after additional process steps of:-

i) dipping the dried CABL latex coated films from step – F) into coagulant bath of step – C;

ii) drying the coagulant coated film of step – i) as per above step – D);

iii) dipping the dried coagulant coated film from step – ii) into neoprene latex bath;

iv) drying the neoprene latex coated coagulated films of step – iii) as per step – F; and

wherein:

v) latex bath of step – E) consists of carboxylated acrylonitrile butadiene latex and no other latex;

vi) the neoprene latex of step – iii) is selected from group consisting of compounded neoprene latex and adhesive grade neoprene latex.

Accordingly, the present invention also relates to a process for preparation of a seamless bladder for an inflatable ball, wherein valve body is adhered or bonded to seamless bladder body, and wherein seamless bladder body is made from carboxylated acrylonitrile butadiene latex and no other latex and is provided with coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex. In accordance with present invention, the valve body is adhered or bonded to said seamless bladder body with coating of natural rubber based adhesive.

In accordance with one of the embodiments of the present invention, it relates to a process for manufacturing of a bladder, wherein it does not get tear-off from its neck during stripping from a mould, and hence, it does not have stripping problem.

In accordance with one of the preferred embodiments, the present invention relates to a process for manufacturing a bladder, wherein it does not have drying problem, and therefore, does not have cracks in the bladder.

In accordance with one of the embodiments of the present invention, the process steps of dipping in coagulant bath and latex bath may be repeated more than once, preferably it is repeated twice.

Accordingly, the advantages of process of present invention include avoiding repeated steps of coating of primer and neoprene rubber adhesive, and repeated steps of heating thereof to dry the coatings, and therefore, overcomes above-described problems of industrial production of inflatable football from bladder of PCT'85.

In accordance with one of the preferred embodiments of the present invention, the process step of dipping the moulds in a coagulant bath in above step – C) is carried out while these are hot and having a temperature varying from about 50^0C to 70^0C, and

the coagulant bath is maintained at a temperature varying from about 20^0C to about 80^0C.

In accordance with one of the preferred embodiments of the present invention, the process step of dipping the dried and coagulant coated formers (in above step – E)) in a compounded latex bath of carboxylated acrylonitrile butadiene latex is carried out when it is maintained at a temperature varying from about 10^0C to 30^0C.

In accordance with one of the preferred embodiments of the present invention, the process step of dipping the dried and coagulant coated film from above step – ii) into neoprene latex bath (in above step – iii)) is carried out when it is maintained at a temperature varying from about 10^0C to 30^0C, and this step is preferably carried out for about 5 seconds to about 2 minutes.

In accordance with one of the preferred embodiments of the present invention, the neoprene latex is compounded neoprene latex.

In accordance with one of the embodiments of the present invention, the [first] coagulant bath for first dip comprises:-

- coagulating agent varying from about 10 parts to about 90 parts by weight of the total weight of the bath composition;
- parting agent varying from about 2 parts to about 8 parts by weight of the total weight of the bath composition; and
- optionally comprising a wetting agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition; and
- optionally comprising a conventional defoamer or surface active agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition;

which are dissolved in water.

In accordance with one of the preferred embodiments of the present invention, the coagulant bath for first dip comprises:-

- coagulating agent, which is preferably calcium chloride or calcium nitrate;
- parting agent, which is preferably bentonite clay; and
- optionally comprising a wetting agent, which is preferably non-ionic group.

In accordance with one of the embodiments of the present invention, the [second] coagulant bath for second or subsequent dips comprises:-

- coagulating agent varying from about 10 parts to about 90 parts by weight of the total weight of the bath composition; and
- optionally comprises a wetting agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition; and
- optionally comprises a conventional defoamer or surface active agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition;

which are dissolved in water.

In accordance with one of the preferred embodiments of the present invention, the coagulant bath for second or subsequent dips comprises:-

- coagulating agent, which is preferably calcium chloride or calcium nitrate; and
- optionally comprises a wetting agent, which is preferably non-ionic group.

In accordance with one embodiment of the present invention, the carboxylated acrylonitrile butadiene latex bath for all dips comprises dry parts of:-

- carboxylated acrylonitrile butadiene latex about 100 phr [per hundred rubber];
- ph modifier varying from about 0.3 to about 0.8 phr;
- surfactants varying from about 0.1 to about 3.0 phr;
- activator and vulcanizing agent varying from about 0.5 to about 5 phr;
- ultra fast accelerator varying from about 1 to about 3 phr;
- vulcanizing agent varying from about 0.25 to about 3.0 phr;
- plasticizer varying from about 1 to about 6 phr;
- antioxident varying from about 1 to about 3 phr; and
- optionally comprising one or more of conventional colours,

which are dissolved in water to have 25 to 55% of compounded latex bath.

In accordance with one of the preferred embodiments of the present invention, the carboxylated acrylonitrile butadiene latex bath for all dips comprises:-

- a ph modifier which is preferably about 2 to 3% potassium hydroxide [KOH] solution;
- a surfactant which is selected from a group comprising anionic group;

- an activator and vulcanizing agent which is preferably 50% dispersion of zinc oxide;
- an ultra fast accelerator which is preferably 50% dispersion of zinc diethyl dithiocarbamate [ZDEC] or of zinc dibutyl dithiocarbamate [ZDBC];
- a vulcanizing agent which is preferably 50% dispersion of sulphur or 33% dispersion of diphenilthiourea [DPTU];
- a plasticizer which is preferably 50% emulsion of dioctylephthalate;
- a antioxidant which is preferably 50% dispersion or emulsion of phenol, amine, aniline or hydroquinone.

In accordance with this invention, the parting agent is not added in the second coagulant bath which has been found to have advantage of avoiding delamination of the subsequent film.

In accordance with one embodiment of the present invention, the carboxylated acrylonitrile butadiene latex is characterized by:-

- acrylonitrile copolymer with medium or high acrylonitrile level varying from about 26% to about 39%;
- solid content varying from about 39% to about 50% of dry rubber contents;
- pH value varying from about 7.5 to about 8.5;
- viscosity varying from about 14 to about 65 mPas;
- surface tension varying from about 30 to about 40 mN/m.

In accordance with one of the preferred embodiments of the present invention, the compounded neoprene latex comprises:

Neoprene latex	–	about 100 Phr,
Stabilizer	-	about 0.1 – 1 Phr,
Antioxidant	-	about 0.5-2 phr,
Activator	-	about 2.0-10 phr,
Accelerator-I	-	about 0.5-3 phr,
Accelerator-II	-	about 0.2-1 phr,
Vulcanizing Agent	-	about 0.25-3 phr,
Pigment	-	about 0.1-2 phr,

In accordance with one of the preferred embodiments of the present invention, in the compounded neoprene latex,

the neoprene latex is preferably film grade,

the stabilizer is preferably lissapol D paste (a sulphated fatty alcohol) which is preferably taken as 20% solution,

the antioxidant is preferably TQ- (polymerized 1,2 dihydro 2,2,4-trimethyl quinoline),

the activator is preferably zinc oxide which is preferably taken as 50% dispersion,

the Accelerator-I is preferably zinc diethyl dithiocarbamate [ZDC] which is preferably taken as 50% dispersion,

the Accelerator-II is preferably diphenyl thiourea [DPTU] which is preferably taken as 25% dispersion.

In accordance with one of the preferred embodiments of the present invention, the water, preferably distilled water is added to the compounded neoprene latex to reduce or adjust its viscosity.

In accordance with one of the preferred embodiments of the present invention, the concentration of neoprene latex bath preferably varies from about 20 to about 40% (DRC).

In accordance with one of the preferred embodiments of the present invention, the coagulant latex bath composition and concentration thereof for neoprene latex bath is same as that of CABL coagulant bath.

In accordance with one of the preferred embodiments of the present invention, the moulds [or formers] are rinsed in a weak acid bath of an acid selected from acetic acid or nitric acid having acid bath concentration varying from about 2% to 4% by weight in luke warm water.

In accordance with one of the preferred embodiments of the present invention, the rinsed formers obtained from preceding process step are dipped in hot water maintained at a temperature varying from about 40^0C to about 90^0C to heat the moulds [formers] and to further clean them by removal of acid traces therefrom.

In accordance with one of the preferred embodiments of the present invention, the coagulant coated formers obtained from preceding process step are dried in hot air tunnel for a duration varying from about 15 sec to 5 min or at room temperature till the formers get fully dried.

In accordance with one of the preferred embodiments of the present invention, the second or subsequent coagulant coated latex films obtained from preceding process

step are dried in hot air tunnel for a duration varying from about 15 sec to 15 min or at room temperature till the films get fully dried.

In accordance with one of the preferred embodiments of the present invention, the substantially dried latex coated coagulated film obtained from preceding process step is subjected to process steps of beading onto neck portion of the former to form a bead which has been found to facilitate its easy stripping without tearing-off at the neck portion followed by leaching in hot water bath to remove excess of unwanted chemicals.

In accordance with one of the preferred embodiments of the present invention, the vulcanized bladders are subjected to accelerated cooling and washing by sprinkling of cold water for a period varying from about 5 to about 10 min.

In accordance with one of the preferred embodiments of the present invention, the cooled and washed bladder shells are striped manually from the respective moulds [formers].

In accordance with one of the preferred embodiments of the present invention, the bladder shells are washed with luke warm water in a centrifuge chamber at a temperature varying from 40^0C to 60^0C to remove clay and other unwanted material.

In accordance with one of the preferred embodiments of the present invention, the washed bladder shells are dried in hot air tumbler for about 30 to 180 min at a temperature varying from 50^0C to 100^0C to remove water contents therefrom.

In accordance with one of the preferred embodiments of the present invention, the valve body is fixed onto the bladder shells, preferably at the neck portion and it is sealed to provide air tight joint and to form a bladder suitable for an inflatable ball.

Experimental Studies:

The inventors have found that the football made from the bladder of carboxylated acrylonitrile butadiene latex having a coating of compounded neoprene latex [NL] or of adhesive grade neoprene latex provided with a valve body having a coating of natural rubber based adhesive has judicious combination of good air retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

Additionally, the inventors have also found substantial reduction in problems and risk of rejection during buffing of the bladder of present invention before adhering or bonding the valve body thereon.

Therefore, the advantages of present invention include additional gain by substantial reduction of loss of production due to rejection during buffing.

The inventors have found that when a test piece of about 25mm wide and about 152.4mm long having on one end an opening of about 25mm, angle of separation during peeling of about 180^0, was tested on a tensile testing machine of about 250Kg, wherein the speed is kept constant and the load taken to separate the test piece upto about 25mm is recorded, the rate of movement of transverse driven grip is kept at about 50 ± 5cm per minute, the adhesion property of valve body onto the bladder body of the ball made as per present invention and as per invention of PCT'85 (the comparative sample), as provided in Table – I, clearly and unambiguously, confirm that adhesion property of the ball made as per present invention is, surprisingly and unexpectedly, substantially increased by an average of about 32.22% in-addition to having advantages of the overall manufacturing process of present invention being easy and simple (i.e. having less number of process steps), and having favourable economics.

Table I

Type of Bladder Body	**Type of Valve Body**	**Type of Adhesive Material on Valve Body**	**Adhesion Property**
As per PCT'85 of Carboxylated Acrylonitrile Latex and no other latex (The Prior Art)	Natural Rubber	*Multiple coatings* of imported primer & neoprone rubber solution	2.25 Kg/Cm^2 2.60 Kg/Cm^2 2.32 Kg/Cm^2
Average value			2.39 Kg/Cm^2
Carboxylated Acrylonitrile Latex coated with Neoprone Latex* (The present Invention)	Natural Rubber	*Single coating* of natural rubber based adhesive	3.10 Kg/Cm^2 3.23 Kg/Cm^2 3.15 Kg/Cm^2
Average value			3.16 Kg/Cm^2

* compounded neoprene latex [NL] or adhesive grade neoprene latex.

Accordingly, it is understood from the foregoing that advantages of present invention include substantially reduced production cost by reducing process time, process cost and rejection rate, and by increasing the productivity, and the bladder is still

suitable for hand stitched as well as machine stitched inflatable balls, and has judicious combination of good air retention characteristics as well as good bounce characteristics without sacrificing one property for the another property.

Accordingly, the overall process of present invention is highly economical on industrial scale.

Claims:

1. A seamless bladder having improved adhesion for valve body or improved capability to bond with valve body,

wherein the bladder comprises

a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex,

wherein said bladder body is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex.

2. A seamless bladder as claimed in claim 1, wherein said bladder is suitable for hand stitched and machine stitched inflatable balls.

3. A seamless bladder as claimed in claim 1 or 2, wherein said bladder body is additionally provided with a valve body.

4. A seamless bladder as claimed in any one of preceding claims 1 to 3, wherein said coating on said bladder body is of thickness varying from about 0.02 mm to about 0.20 mm, preferably of thickness varying from about 0.03 mm to about 0.15 mm.

5. A hand stitched or machine stitched inflatable ball made from seamless bladder,

wherein said seamless bladder comprises a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, and

said bladder body is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex.

6. A ball as claimed in claim 5, wherein said bladder body is provided with a valve body.

7. A ball as claimed in claim 6, wherein said valve body is adhered or bonded to said bladder body with at least one coating of natural rubber based adhesive.

8. A ball comprising:

a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body,

wherein said seamless bladder comprises

a bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, and

wherein said bladder body is provided with at least one coating of a material selected from group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, and

wherein said seamless bladder body is provided with a valve body,

wherein said valve body is provided with at least one coating consisting of natural rubber based adhesive, and

wherein said valve body is adhered or bonded with (or to) said bladder body.

9. A hand stitched and machine stitched inflatable ball comprising:

i) seamless bladder body made from carboxylated acrylonitrile butadiene latex and no other latex, wherein said bladder body consisting of carboxylated acrylonitrile butadiene latex is provided with at least one coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex, and

ii) valve body adhered or bonded to said seamless bladder body, wherein said valve body is adhered or bonded to said bladder body with at least one coating consisting of natural rubber based adhesive.

10. A ball as claimed in any one of the preceding claims 5 to 9, wherein said coating of a material selected from a group consisting of compounded neoprene latex [NL] and adhesive grade neoprene latex on said bladder body is of thickness varying from about 0.02 mm to about 0.20 mm, preferably varying from about 0.03 mm to about 0.15 mm.

11. A ball as claimed in any one of the preceding claims 5 to 10, wherein said coating consisting of natural rubber based adhesive on said valve body is of thickness varying from about 0.005 mm to about 0.03 mm, preferably of thickness varying from about 0.01 mm to about 0.015 mm.

12. A process for manufacture of a seamless bladder having improved adhesion for valve body or improved capability to bond with valve body, wherein the process comprises steps of:

A) cleaning the multiple moulds by rinsing in an acid bath;

B) heating the rinsed formers obtained from process step – A) by dipping in hot water;

C) dipping the heated moulds from process step – B) in a coagulant bath;

D) drying the coagulant coated formers obtained from process step – C);

E) dipping the dried and coagulant coated formers obtained in process step – D) in compounded latex bath of carboxylated acrylonitrile butadiene latex [CABL];

F) drying the latex coated coagulated films obtained from process step – E);

G) beading the substantially dried latex coated coagulated films obtained from process step– F) to form a bead followed by leaching;

H) drying and vulcanizing the leached formers with bladder obtained from process step – G);

I) cooling and washing the vulcanized bladders obtained from process step – H); and

J) stripping the cooled and washed bladders obtained from process step – I) from the respective moulds [formers];

characterized in that

the process step - G) is performed after additional process steps of:-

i) dipping the dried CABL latex coated films from step – F) into coagulant bath of step – C;

ii) drying the coagulant coated film of step – i) as per above step – D);

iii) dipping the dried coagulant coated film from step – ii) into neoprene latex bath;

iv) drying the neoprene latex coated coagulated films of step – iii) as per step – F; and

wherein:

v) latex bath of step – E) consists of carboxylated acrylonitrile butadiene latex and no other latex;

vi) the neoprene latex of step – iii) is selected from group consisting of compounded neoprene latex and adhesive grade neoprene latex.

13. A process as claimed in claim 12, wherein said process steps of dipping in coagulant bath and latex bath may be repeated more than once, preferably it is repeated twice.

14. A process as claimed in claim 12 or 13, wherein said process step of dipping the moulds in a coagulant bath in said step – C) is carried out while these are hot and having a temperature varying from about 50^0C to 70^0C, and the coagulant bath is maintained at a temperature varying from about 20^0C to about 80^0C.

15. A process as claimed in any one of preceding claims 12 to 14, wherein said process step of dipping said dried and coagulant coated formers in said step – E) in said compounded latex bath of carboxylated acrylonitrile butadiene latex is carried out when it is maintained at a temperature varying from about 10^0C to 30^0C.

16. A process as claimed in any one of preceding claims 12 to 15, wherein said process step of dipping said dried and coagulant coated film from said step – ii) into neoprene latex bath of said step – iii) is carried out when it is maintained at a temperature varying from about 10^0C to 30^0C.

17. A process as claimed in claim 16, wherein said process step is preferably carried out for about 5 seconds to about 2 minutes.

18. A process as claimed in any one of preceding claims 12 to 17, wherein said neoprene latex is preferably compounded neoprene latex.

19. A process as claimed in any one of preceding claims 12 to 18, wherein said [first] coagulant bath for first dip comprises:-

- coagulating agent varying from about 10 parts to about 90 parts by weight of the total weight of the bath composition;
- parting agent varying from about 2 parts to about 8 parts by weight of the total weight of the bath composition; and
- optionally comprising a wetting agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition; and
- optionally comprising a conventional defoamer or surface active agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition;

which are dissolved in water.

20. A process as claimed in any one of preceding claims 12 to 19, wherein said coagulant bath for first dip comprises:-

- coagulating agent, which is preferably calcium chloride or calcium nitrate;

- parting agent, which is preferably bentonite clay; and
- optionally comprising a wetting agent, which is preferably non-ionic group.

21. A process as claimed in any one of preceding claims 12 to 20, wherein said [second] coagulant bath for second or subsequent dips comprises:
- coagulating agent varying from about 10 parts to about 90 parts by weight of the total weight of the bath composition; and
- optionally comprises a wetting agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition; and
- optionally comprises a conventional defoamer or surface active agent varying from about 0.01 parts to about 0.5 parts by weight of the total weight of the bath composition;

which are dissolved in water.

22. A process as claimed in any one of preceding claims 12 to 21, wherein said coagulant bath for second or subsequent dips comprises:
- coagulating agent, which is preferably calcium chloride or calcium nitrate; and
- optionally comprises a wetting agent, which is preferably non-ionic group.

23. A process as claimed in any one of preceding claims 12 to 22, wherein said carboxylated acrylonitrile butadiene latex bath for all dips comprises dry parts of:-
- carboxylated acrylonitrile butadiene latex about 100 phr [per hundred rubber];
- ph modifier varying from about 0.3 to about 0.8 phr;
- surfactants varying from about 0.1 to about 3.0 phr;
- activator and vulcanizing agent varying from about 0.5 to about 5 phr;
- ultra fast accelerator varying from about 1 to about 3 phr;
- vulcanizing agent varying from about 0.25 to about 3.0 phr;
- plasticizer varying from about 1 to about 6 phr;
- antioxident varying from about 1 to about 3 phr; and
- optionally comprising one or more of conventional colours,

which are dissolved in water to have 25 to 55% of compounded latex bath.

24. A process as claimed in any one of preceding claims 12 to 23, wherein said carboxylated acrylonitrile butadiene latex bath for all dips comprises:
- a ph modifier which is preferably about 2 to 3% potassium hydroxide [KOH] solution;
- a surfactant which is selected from a group comprising anionic group;
- an activator and vulcanizing agent which is preferably 50% dispersion of zinc oxide;
- an ultra fast accelerator which is preferably 50% dispersion of zinc diethyl dithiocarbamate [ZDEC] or of zinc dibutyl dithiocarbamate [ZDBC];
- a vulcanizing agent which is preferably 50% dispersion of sulphur or 33% dispersion of diphenilthiourea [DPTU];
- a plasticizer which is preferably 50% emulsion of dioctylephthalate;
- a antioxidant which is preferably 50% dispersion or emulsion of phenol, amine, aniline or hydroquinone.

25. A process as claimed in any one of preceding claims 12 to 24, wherein said second coagulant bath does not comprise parting agent.

26. A process as claimed in any one of preceding claims 12 to 25, wherein said carboxylated acrylonitrile butadiene latex has:
- acrylonitrile copolymer with medium or high acrylonitrile level varying from about 26% to about 39%;
- solid content varying from about 39% to about 50% of dry rubber contents;
- pH value varying from about 7.5 to about 8.5;
- viscosity varying from about 14 to about 65 mPas;
- surface tension varying from about 30 to about 40 mN/m.

27. A process as claimed in any one of preceding claims 12 to 26, wherein said compounded neoprene latex comprises:

Neoprene latex	–	about 100 Phr,
Stabilizer	-	about 0.1 – 1 Phr,
Antioxidant	-	about 0.5-2 phr,
Activator	-	about 2.0-10 phr,
Accelerator-I	-	about 0.5-3 phr,
Accelerator-II	-	about 0.2-1 phr,

Vulcanizing Agent	-	about 0.25-3 phr,
Pigment	-	about 0.1-2 phr,

28. A process as claimed in any one of preceding claims 12 to 27, wherein in said compounded neoprene latex

the neoprene latex is preferably film grade,

the stabilizer is preferably lissapol D paste (a sulphated fatty alcohol) which is preferably taken as 20% solution,

the antioxidant is preferably TQ- (polymerized 1,2 dihydro 2,2,4-trimethyl quinoline),

the activator is preferably zinc oxide which is preferably taken as 50% dispersion,

the Accelerator-I is preferably zinc diethyl dithiocarbamate [ZDC] which is preferably taken as 50% dispersion,

the Accelerator-II is preferably diphenyl thiourea [DPTU] which is preferably taken as 25% dispersion.

29. A process as claimed in any one of preceding claims 12 to 28, wherein water is added to said compounded neoprene latex to reduce or adjust its viscosity.

30. A process as claimed in any one of preceding claims 12 to 29, wherein concentration of said neoprene latex bath preferably varies from about 20 to about 40% (DRC).

31. A process as claimed in any one of preceding claims 12 to 30, wherein said coagulant latex bath composition and concentration thereof for neoprene latex bath is same as that of CABL coagulant bath.

32. A process as claimed in any one of preceding claims 12 to 31, wherein said seamless bladder is provided with a valve body, which is adhered or bonded to said seamless bladder body with a coating consisting of natural rubber based adhesive.

33. A seamless bladder and a ball comprising said seamless bladder and process for manufacture thereof substantially as herein described with the help of foregoing examples.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2012/000564

A. CLASSIFICATION OF SUBJECT MATTER
INV. A63B41/02 A63B41/00 A63B45/00 B29C41/14 C08L9/04
ADD.

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)
A63B B29C C08L

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/107914 A2 (PARADISE RUBBER IND [IN]; MAGON PREM NATH [IN]; MAGON ASHWANI [IN]) 12 September 2008 (2008-09-12) page 1, line 5 - page 25, line 6 claims 1-36	1-32
A	WO 03/006513 A1 (BEST MFG COMPANY [US]; WILLIAMS WILLIAM ANDRUS [US]; CLEVELAND JOYCE L) 23 January 2003 (2003-01-23) page 3, line 30 - page 11, line 25	1-32
A	US 4 513 058 A (MARTIN ROBIN A [US]) 23 April 1985 (1985-04-23) column 2, line 6 - column 5, line 54; figures 1,2	1-32

☐ 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
14 December 2012	02/01/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Jekabsons, Armands

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2012/000564

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 33
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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. ☐ 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 an 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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 33

Present claim 33 relates to an extremely large number of possible apparatus, such that no meaningful search is possible (Article 6 PCT and Rule 6.2 PCT).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IN2012/000564

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008107914 A2	12-09-2008	NONE	
WO 03006513 A1	23-01-2003	EP 1412395 A1	28-04-2004
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		US 4513058 A	23-04-1985
		ZA 8500570 A	25-09-1985