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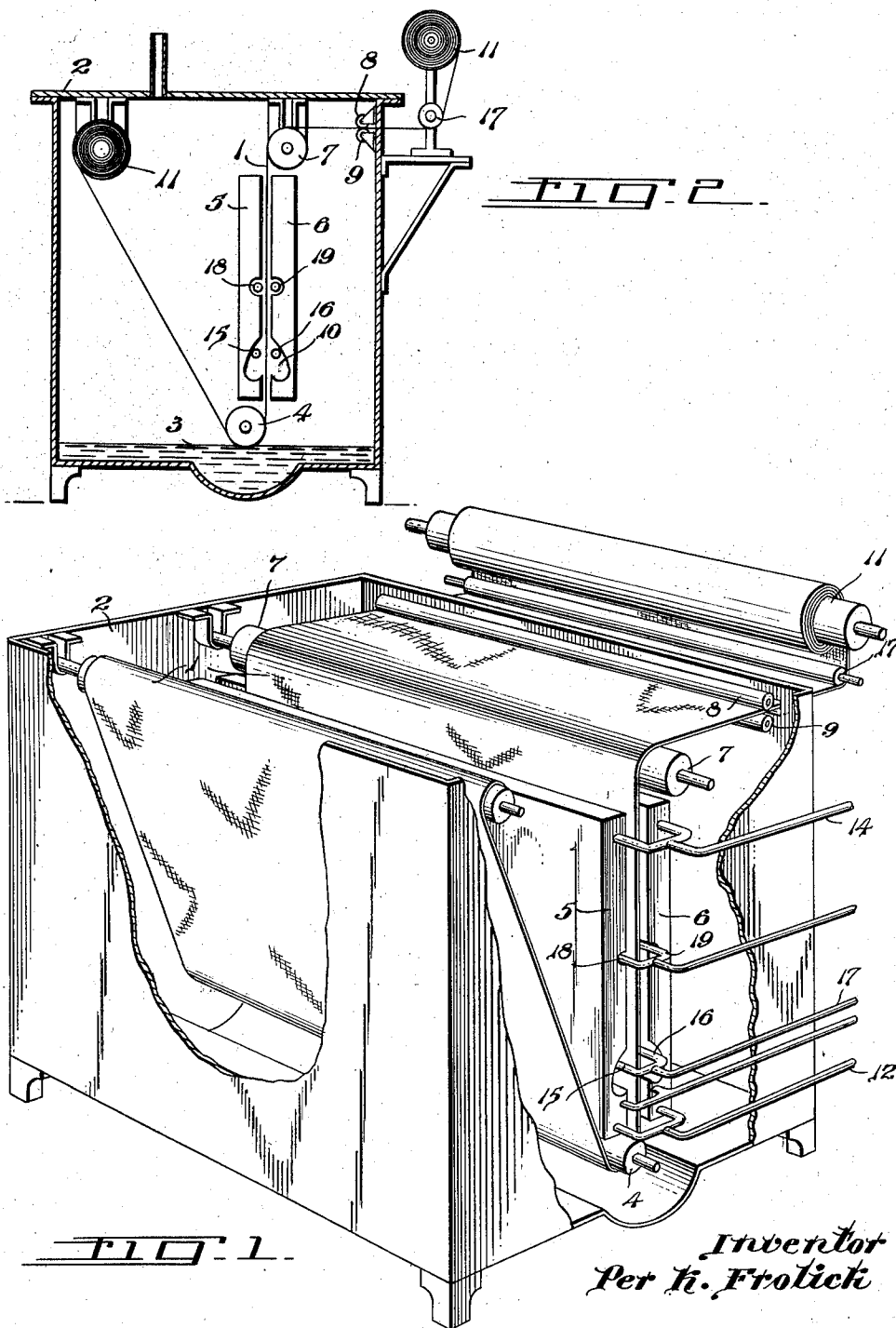
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2,270,285

IMPREGNATED FABRIC

Filed Dec. 31, 1938

2 Sheets-Sheet 1



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FIG. 4.

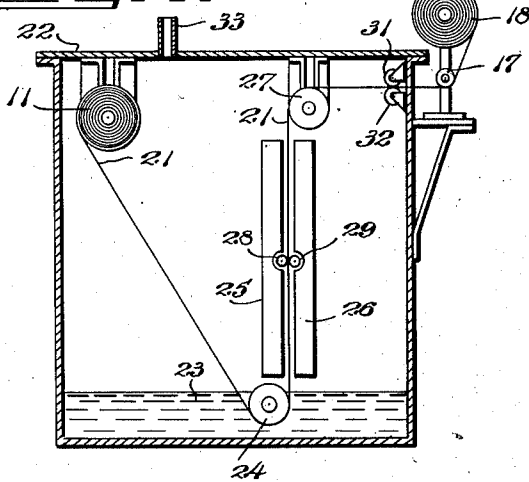


FIG. 5.

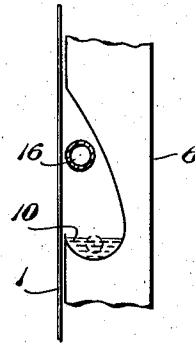
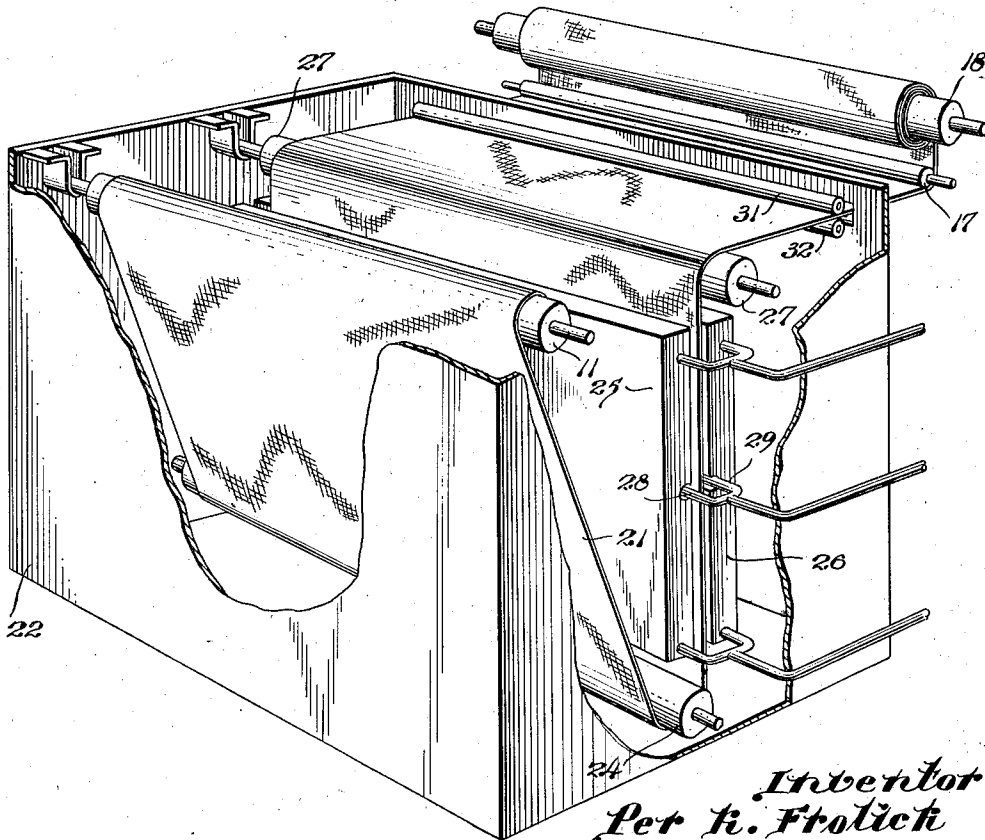


FIG. 3.



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UNITED STATES PATENT OFFICE

2,270,285

IMPREGNATED FABRIC

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Application December 31, 1938, Serial No. 248,793

2 Claims. (Cl. 91—68)

This invention relates to composite fabrics, and particularly to fabrics having as a part thereof, a polymer formed from olefinic hydrocarbons condensed directly in and upon the fibres of the fabric.

For many purposes it is desirable that fabrics of various sorts shall have applied thereto suitable coating substances for such purposes as waterproofing the fabric, filling the interstices between the fibres and threads of the fabric; for protecting the fabric against the attack of destructive elements; for use as a foundation to carry other substances; for pneumatic tire bases, etc., but difficulty has been encountered in getting a wholly satisfactory incorporation of the coating substance into the fabric.

The present invention provides means for polymerizing an olefinic gas directly in and upon the fibres and threads of the fabric, to produce a solid coating and polymer of high molecular weight whereby a particularly thorough, efficient and satisfactory incorporation of the coating material or polymer with respect to the fabric is obtained.

By the procedure of the invention the polymerizable olefinic hydrocarbon and the polymerizing catalyst are applied directly to the fabric, and the polymerization occurs after the olefin and catalyst are in contact with the fabric to produce the desired coating of polymerized olefinic substance in particularly intimate contact and association with the fibres and threads of the fabric. Thus an object of the invention is to polymerize an olefinic substance directly upon, and in the presence of, the fibres of a fabric.

This process is also adapted to be used in coating and impregnating other fibrous materials such as paper, wood, leather, building materials, asbestos, mineral wool, slag wool, cotton, "Cello-tex," "Cellophane," viscose, rayons and the like.

Other objects and details of the invention will be apparent from the following description when read in connection with the accompanying drawings wherein

Fig. 1 is a diagrammatic representation of apparatus for polymerizing the olefin upon the fibres of the fabric;

Fig. 2 is a view in section of the embodiment of Fig. 1;

Fig. 3 is an alternative device for practicing the invention;

Fig. 4 is a view in section of the embodiment of Fig. 3; and

Fig. 5 is a detail view of the chill box, spray tube and gutter.

Referring to Figs. 1 and 2, the fabric which is to be impregnated with polymer material may be inserted in the form of a roll or spool 1 within a chill tank 2. The tank 2 may conveniently be cooled by a pool 3 of liquefied ethylene or other suitable refrigerant in the bottom thereof. The fabric from the roll 1 is drawn under a guide roll 4, placed a short distance above the surface of the pool of refrigerant 3 and thence between chill boxes 5 and 6. These chill boxes are desirably filled with liquid ethylene at atmospheric pressure thereby setting the temperature at about -103°C . Alternatively, other refrigerants as desired may be utilized within the chill boxes 5 and 6. The fabric is then desirably drawn over another guide roll 7 above the chill boxes 5 and 6, and from the guide roll 7 between squeeze rolls 8 and 9 to a rewind roll 11.

A supply of ethylene or other refrigerant is delivered to the chill boxes 5 and 6 by way of the supply pipe 12, and the vaporized refrigerant is discharged from the chill boxes 5 and 6 through the pipe 14.

In grooves near the bottom of the chill boxes 5 and 6 there are provided perforated spray pipes 15 and 16 connected to a supply pipe 17 through which there is discharged a supply of cooled olefinic gas which largely condenses in and upon the fabric 1 at the temperature maintained between chill boxes 5 and 6. A short distance above the olefinic gas spray pipes 15 and 16 there are provided other spray pipes 18 and 19 also upon opposite sides of the fabric, through which there is discharged a supply of catalyst which may take the form of gaseous boron trifluoride which is absorbed into the fabric and condensed olefinic gases.

In the presence of the boron trifluoride, the condensed olefinic material polymerizes rapidly into a high molecular weight, substantially saturated, linear type hydrocarbon. The pipes 18 and 19 are desirably placed at a point above the point of entrance of the fabric 1 between the chill boxes 5 and 6 in order that the fabric may be chilled to its lowest temperature before the catalyst comes into contact with the polymerizable olefinic gas charged fabric. It is desirable that as nearly as possible all of the polymerizable olefin shall condense upon fabric 1 rather than upon the walls of the chill boxes 5 and 6. However, since the olefinic material is practically exclusively in the fabric, relatively little harm is done by a contact of the polymerizable olefinic gas with the walls of the chill boxes 5 and 6. It is further desirable that the spray pipes

18 and 19 for the catalyst should be placed a small distance above the spray pipes 15 and 16, in order that substantially all of the olefinic gases may be condensed into and on the fabric before the catalyst is applied to the olefinic material and fabric. This is particularly desirable to avoid danger of condensation and polymerization of the olefinic material upon the walls of the chill tanks 5 and 6.

Such portion of the olefinic gases as are condensed upon the inner surface of the chill boxes 5 and 6 may be caught by gutter members 10 and returned to the incoming supply of olefinic gas. It will be observed that this arrangement accurately separates from the catalyst any olefinic gases which do not condense upon the fabric.

At the low temperature existing in the fabric, the polymerization occurs very quickly to produce a polymer substance in the interstices of the fabric. The physical characteristics of the polymer obtainable are subject to very accurate control, through the agency of control of the temperature at which the polymerization occurs. As is well-known, the lower the temperature, especially when the polymerizable olefin is pure isobutylene, the higher the molecular weight of the resulting polymer. That is, if the chill boxes 5 and 6 are maintained at a temperature from -10°C . to -25°C ., a polyisobutylene substance is produced upon the fabric which may have a molecular weight ranging from 5,000 to 25,000 being thereby a plastic, somewhat sticky substance. If the temperature of the chill boxes 5 and 6 is kept within the range from -35°C . to -90°C ., a solid elastic polymer is produced upon the fabric and in the interstices of the fabric which may have a molecular weight ranging from 25,000 to 250,000.

In some instances, especially when it is desired to incorporate a very large amount of polymer material into and onto the fabric, it is preferable to saturate the fabric with the olefinic material in the liquid form, and for this purpose the embodiment of Figs. 3 and 4 may be utilized. In this form of the invention, a pool 23 of condensed olefinic gas is maintained at the bottom of the chill tank 22 as shown, and the fabric 21 is carried under the guide roll 24 and upward between the chill boxes 25 and 26 in a manner closely similar to that previously described. However, only a single pair of spray pipes 28 and 29 is provided, through which the catalyst is discharged onto the olefin-carrying fabric. In this embodiment, the catalyst used may be gaseous boron trifluoride as before described or it may be a solution of aluminum chloride in ethyl chloride. In either event, the polymerization takes place in and on the fabric between the chill boxes.

In still another embodiment of the invention, a pool of liquid catalyst solution 23 may be maintained at the bottom of the chill tank 22 and the fabric 21 may be passed first through the pool of liquid catalyst 23 such as aluminum chloride dissolved in ethyl chloride, or boron trifluoride dissolved in liquefied ethylene or other of the Friedel-Craft type of catalysts. The catalyst-carrying fabric is then drawn upward under the roll 24 between the chill boxes 25 and 26 as before, past the spray tubes 28 and 29 through which the olefinic gas is discharged. The gas condenses upon the fabric and polymerizes therein in the presence of the catalyst.

The polymer-coated fabric may then be drawn

over the roller 27 between a pair of exit rollers 31 and 32 which serve to limit the egress of any unpolymerized olefinic gases from the container 22 and by a wringer action may be caused to return a substantial portion of the catalyst solution to the bottom of the container 22. It is desirable that the catalyst solution 23 be reduced to a minimum temperature, and accordingly a substantial portion of liquid ethylene may be added at atmospheric pressure to the solution 23 to maintain the entire tank 22 and all its contents at the desired low temperature.

The effluent gas which may comprise in large part the refrigerant ethylene, and in further part may comprise unpolymerized olefinic gas, is discharged from the container 22 through an exit pipe 33.

It is not necessary that pure isobutylene be utilized for the polymerizable substance. Instead, a mixture of isobutylene and butadiene may be utilized. This mixture is preferably made in the ratio of 70-90 parts of isobutylene and 30-10 parts of butadiene. The mixture may be condensed into a pool of olefinic liquid 23 at the bottom of the chill tank 2 and the fabric dipped into the pool 23 of the liquefied mixed olefins. When saturated with the olefins, the fabric may be drawn between the chill plates 25 and 26, and the catalyst discharged through the spray pipes 28 and 29 onto the fabric. For this polymerization it is preferable to use the solution of aluminum chloride in ethyl chloride pointed out in the previously described embodiment. Other catalysts may, however, be utilized.

This type of polymerization may be performed from the gaseous phase in common with the previously described form, by the use of two pairs of spray tubes, the lower pair being utilized to discharge onto and into the fabric a gaseous mixture of the desired olefins, which are then condensed by the abstraction of the heat of vaporization into the chill tanks 25 and 26 and the catalyst is sprayed onto the fabric from the second pair of spray tubes. If a small amount only of polymer is to be incorporated into the fabric, it is desirable that a substantial portion of the olefinic gases shall be absorbed into the fabric before polymerization, in order to permit of the completion of the polymerization. When larger quantities of the polymer are to be laid down upon the fabric a portion of the polymerization may occur simultaneously with the condensation of the material into the fabric although this latter arrangement is less satisfactory since it does not insure permeation of all of the polymer into the fabric as effectively as is possible when the olefinic material penetrates into the fabric before the polymerization reaction begins.

It is to be noted that the polymerization reaction is exceedingly sensitive to poisoning by included substances, and it has been found that a high molecular weight polymer is obtainable only when the polymerization is conducted with exceedingly pure olefinic gas, and a very pure catalyst. Even small traces of a wide range of substances act as catalyst poisons, and either prevent the polymerization entirely, or reduce it to such a low amount as to produce nothing but a low molecular weight polymer which is merely a liquid, viscous oil. In contrast to the active poisoning effect resulting from the presence of most auxiliary substances, it is found that cellulosic materials are substantially free from poisoning effect upon the catalytic polymerization reaction; and that the polymerization occurs just as readily

in the presence of cellulose material as in the absence of impurities of all sorts.

Furthermore, it is found that the polymer is exceedingly closely attached to the cellulosic fibres; and far more closely attached than is possible with any of the calendering or dipping treatments previously utilized for the application of various gums, waxes, resins, etc., to fabrics. It has not been possible as yet to prove that an interpolymerization occurs between the polymerizing olefinic gas and the cellulose molecule, but to the present it has not been possible to show that no such interpolymerization occurs, and it may well be that some such reaction takes place. Furthermore, it is well established that cellulose occurs in the form of very large molecules which in a cellulose fibre occur in "micellae" which are oriented in the fibre in a definite manner. It is believed that whether interpolymerization between the cellulose molecule and olefinic gas occur or not, a substantial penetration of the polymer into the micellar structure of the cellulose occurs, thereby producing a far more intimate interrelationship between the cellulose and olefinic polymer than is possible by any other procedure.

In any event the resulting fabric shows all of the resistance to acid, alkali, oxygen and other chemical action which is characteristic of the polymer per se, and the cellulose in the fabric appears to be far more thoroughly protected than is possible with any other type of coating or impregnating treatment.

Furthermore, the amount of polymer present is readily determined by the rate at which the polymerizable olefinic gas is delivered into the fabric, or the amount of liquefied olefinic material which is charged into the fabric before polymerization. The quantity may be controlled between an amount sufficient to produce a fully impervious sheet closely analogous to balloon cloth, or a fully impregnated tire cord fabric which is fully covered including a relatively thick surface layer, down to an amount so small as to be practically imperceptible to touch or observation, but sufficient to give the fabric a new and valuable springy characteristic, and still provide a pronounced and valuable protection against oxidation or other chemical reactions of the cellulose fibre.

It is well known that the isobutylene polymer, especially when produced to have a molecular weight ranging from 27,000 to 300,000, is exceedingly resistant to atmospheric oxygen; to oxygen-containing solvents, to acids, to alkali, and to heat if not excessive, and accordingly a fabric having very greatly increased wear-resisting properties is obtainable.

These qualities are particularly characteristic of the polymer produced from the mixture of isobutylene and butadiene which when sulfurized as described below has a resistance to heat, to abrasion, and to flexure which is outstandingly superior to any other analogous substances. That is, it is possible to iron the fabric without injury to the polymer coating. Furthermore, the material does not oxidize in air to become stiff, brittle and harsh; and the presence of the polymer material provides a very valuable lubricating effect between the fibres of the fabric.

A particularly valuable product is obtainable when the gas discharged through the pipes 11 and 12 consists of 80% to 90% isobutylene and from 20% to 10% butadiene. It is of course desirable that the catalyst be removed from the

polymer material. This is readily accomplished by washing and kneading the material in water or alkaline solution or by other methods which will be obvious to workers in the field. This material can be sulfurized, and a sufficient amount of sulfur for the reaction may be incorporated into the fabric either from suspension or solution in the liquid catalyst, if such is used, or by sprinkling the sulfur in a form such as flowers of sulfur upon the fabric after the polymerization procedure. The sulfurization may then be completed by heating the fabric and incorporated polymer to a temperature in the neighborhood of 140° C. for the required length of time of several hours.

The procedure of the invention is particularly advantageous for reinforcing fabric used in automobile tires, especially when the tread is produced from the same polymer of isobutylene-butadiene since under these circumstances a particularly thorough and effective incorporation of the polymer into the fabric is obtainable; and since the polymer is a linear chain hydrocarbon, it provides a very valuable lubricating effect between the fibres of the fabric which greatly lengthens the life of the fabric and tire produced therefrom and reduces the rate of wear in service.

The above-described embodiments are presented as incorporating the polymer material into a cotton fabric. It is not, however, limited to spun and woven cotton fabrics since the reaction proceeds equally satisfactorily with linen fabrics, which are chemically cellulose in slightly different physical form from cotton fibres. The polymerization procedure is similarly adapted to the impregnation of woollen fabrics with polymer in any desired amount; and to the impregnation of silk fabrics. It is particularly advantageous for this purpose, since a small amount of the polymer provides a very valuable stiffening, strengthening and wear-reducing effect which is far superior to the practice of weighting by means of tin. The amount of polymer may be just sufficient to coat the silk filaments without noticeably modifying the appearance, and modifying the feel of the silk only to the extent of slightly increasing the springiness or stiffness; or larger amounts may be incorporated to give considerably increased springiness and elasticity, up to the point where a fully waterproof fabric is produced. The process is equally applicable to rayon, either of the viscose type, the cuprammonium type, or the denitrified Chardonnet type, these being all regenerated cellulose or hydrocellulose, and the procedure is similarly effective. The procedure is equally applicable to the celanese type of artificial silk which is spun cellulose acetate. The procedure is also applicable to felts, whether formed of fur or wool; and to paper as well. The procedure is also applicable to sheet Cellophane for the production of a strongly adherent waterproof and wear-resistant coating upon one or both surfaces of the Cellophane. The procedure is readily applicable to the very thinnest fabrics, such as tulle or veiling or georgette; or to the very heaviest fabrics, such as canvas or woollen suiting as well as to velvet either upon the back only and in small quantity, or throughout the velvet. This procedure when applied to velvet is particularly valuable because it produces a fully crushproof velvet which has been previously unobtainable. The procedure is also applicable to such fabrics as leather, and also to felted or spun and woven asbestos and similar fabrics.

There is thus produced by the process and apparatus of the invention a new type of fabric in which there is polymerized a substantial quantity of an olefinic substance to form a high molecular weight polymer which is extremely thoroughly interspersed between the fibres of the fabric. When so dispersed the polymer provides an amount of protection for the fibres which is of a wholly new order of magnitude both by virtue of the fact that the fibres are sheathed with chemically inert and resistant polymer in a fashion not previously possible; and by virtue of the lubricating effect of the polymer between the fibres of the fabric. The invention thus provides a process for incorporating polymer into a fabric; a machine for facilitating the incorporation of the polymer into the fabric; and a new material comprising a fabric having an olefinic polymer exceedingly intimately incorporated into the fibres thereof.

While there are above disclosed but a limited number of embodiments of the structure of the invention, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is therefore desired that only such limitations be imposed

upon the appended claims as are stated therein or required by the prior art.

The invention claimed is:

1. The process of producing a high molecular weight heteropolymer of isobutylene and butadiene in the interstices of a fabric which comprises the steps of charging the fabric with a mixture of isobutylene and butadiene, and treating the charged fabric with a Friedel-Crafts type catalyst at a temperature below -10°C. , thereby polymerizing the mixture of isobutylene and butadiene to a high molecular weight polymer in the interstices of the fabric.

2. The process of producing a high molecular weight heteropolymer of isobutylene and butadiene in the interstices of a fabric which comprises the steps of charging the fabric with a mixture of isobutylene and butadiene, and treating the charged fabric with a Friedel-Crafts type catalyst comprising a solution of aluminum chloride in a non-complex-forming solvent which is liquid below -10°C. , thereby polymerizing the mixture of isobutylene and butadiene to a high molecular weight polymer in the interstices of the fabric.

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