PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in Shaped Bodies, such as Thin Sheets, Threads or the like, Composed Essentially of Rubber Hydrochloride and Methods of Producing such Bodies

I, HENRY DUDLEY MINICH, of 528, Bellwood Avenue, Phillipse Manor, North Tarrytown, State of New York, United States of America, a citizen of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in shaped bodies such as thin sheets, threads or the like formed essentially of rubber hydrochloride and methods of producing such bodies.

Although the known transparent films and similar flexible bodies composed of rubber hydrochloride surpass similar cellulose bodies in extensibility, tear-resistance, impact strength, resistance to puncturing and breaking as well as resistance to moisture, oils and grease, they are inferior to such cellulose products in tensile strength and also lack lustre crackliness and other properties desirable in such materials.

I have found that films, threads, laminations, and like bodies of known rubber hydrochloride materials which have been stretched in at least one direction exhibit greatly increased tensile strength in the direction of the stretch, compared with unstretched rubber hydrochloride bodies. A stretched rubber hydrochloride body, such as a sheet, thread, and the like, may be produced in accordance with the present invention, by heating such body composed essentially of rubber hydrochloride which is solid at room temperature to an elevated temperature at which it is rendered plastic and stretching it while plastic until at least one of its dimensions is materially increased and cooling in the stretched condition to solidification temperature.

By heating a plurality of plies composed essentially of rubber hydrochloride to a plastic state and uniting the plies and stretching them while plastic and then allowing them to cool, a stretched lamination is obtained which has greatly increased tensile strength in the direction of the stretch.

Such stretching of known materials consisting essentially of rubber hydrochloride, may be carried on while the composition is rendered plastic by heating it to an elevated temperature in the range between about 120° F. to 230° F.

I have found that stretched rubber hydrochloride material, such as sheets, laminations, and threads obtained by such treatment, although thinner than before treatment, has much greater tear-resistance and, what is more important, has a materially greater tensile strength than the untreated sheet. The heat-treated stretched material acquires a spring-like resiliency, high lustre, and crackly feel indicating that some tension-like character was imparted to the inner structure of the material by the treatment. The texture of the treated compound may be modified within large limits by varying the temperature and the character of the heating process applied to the material, the degree of stretching, the speed with which it is stretched, the support of the material during the heating and stretching, the process of cooling accompanying and following the tensioning process, and the character of the support and the handling means applied to the material during the heating, tensioning and cooling process.

Since the new treatment of rubber hydrochloride materials and the improved products of such treatment are of particular value in making transparent or coloured sheet material superior in tensile and tearing strength, as well as high lustre to the known rubber hydrochloride sheets, this treatment is of special importance in the production of rubber hydrochloride sheet material, and of various new laminated, drawn, twisted rubber hydrochloride sheet material structures having great strength and other desirable characteristics.

I shall now explain how to practise the

[*Price* 1/-]

invention as applied for making stretched sheet material composed of rubber hydrochloride by reference to the single figure of the accompanying drawing which illustrates diagrammatically an apparatus for making such material.

Well-washed crepe rubber is dissolved in benzene in the proportion of 5 to 7 parts of rubber to 100 parts by weight of the solvent. Another suitable solvent, such as chloroform or acetylene-tetrachloride, may be used instead of benzene. The rubber cement solution is maintained at the temperature of about 50° F. while dry hydrochloride gas is passed through the solution for about six hours. This brings about absorption of hydrogen chloride by the rubber solution and the rubber reacts with the hydrogen chloride so that after a further period of about twenty-four hours at room temperature the reaction gives a solution of rubber hydrochloride containing about 29.5% chlorine. The completion of this reaction is checked by testing sample films as to tackiness until the reaction reaches a condition at which the sample film is neither tacky nor brittle, and has the desired characteristics.

After the required state of hydrochlorination of the solution is reached, the solution is subjected to steam distillation, until the solvent and the excess hydrochloric acid are driven off. Instead of steam distillation, the solvent and excess hydrochloric acid may be driven off by passing a dry inert gas, such as nitrogen, or air, through the solution. This may be followed by washing the mass with an ammonia solution to remove remnants of hydrochloric acid which forms ammonium chloride with the solution. The residual mass of rubber hydrochloride obtained from the reaction is washed with water to remove remaining traces of hydrogen chloride and the ammonium chloride and the mass is then dried in a vacuum drier.

To make a rubber hydrochloride film, the product so obtained is again dissolved in a suitable solvent, preferably chloroform, to form a 5% solution by weight. Other solvents may be used for this solution, such as dichlorethylene or acetylene tetrachloride. If the product is to be coloured, a suitable soluble dye is added to the solution, and if the product is to be opaque, insoluble colouring ingredients are added to the solution. To this solution is added a small percentage of a protective organic substance, for instance, 3% by weight of cyclohexylamine formaldehyde, to resist the deterioration of the compound under the action of the sun. Other protective organic substances, such as ditetrahydrofurfurylamine, methyleneaminoacetonitrile and cyclohexylamineacetonitrile may be used instead.

The solution so prepared may be used for making the desired solid rubber hydrochloride product. For producing sheet material, the solution is spread as film on a moving belt, surfaced with a suitable material, such as plastic cellulose acetate or celluloid, and a stream of air is passed over the film to hasten the evaporation of the solvent, leaving a congealed transparent thin film which can be continuously stripped off from the belt as it moves.

The film so prepared is then subjected to a stretching or tensioning treatment by first heating the film to a temperature of about 200° F. at which the film sheet becomes plastic but does not bring about decomposition of the rubber hydrochloride, the heated plastic film being then stretched to increase its length to three to six times its length before heating, and the stretched film is brought back to its lower normal temperature. According to the preferred method of this treatment, the film is fed over a heated surface at a speed which brings the temperature of the film to the desired temperature and the heated film is withdrawn from the heated surface at a speed 2 to 6 times the speed with which it is fed to the heated surface, causing the heated film to be stretched accordingly. As the stretched film is withdrawn from the heating surface it is cooled down and solidified in its tensioned stretched condition.

This treatment can be conveniently carried out by feeding the film that is to be treated through a pair of suitable driven feed rollers to a heating cylinder from which the heated film is withdrawn by stretching rollers driven at a peripheral speed which is a multiple of the peripheral speed of the feeding rollers. The tensioned film is cooled and brought back to a solid state before entering the stretching rollers by a cooling appliance, such as a fan, located in front of the stretching rollers. Although the solid tensioned film delivered by the stretching roller is thinner than the untreated film, its tearing and tensile strength in the longitudinal direction is several times increased. The tensioned stretched film has also a lustre and a crackly feel not present in the untreated film. By this longitudinal stretching process the hydrochloride film acquires in the direction in which it is stretched a tensioned mechanical equilibrium which gives it the new desirable characteristic and a kind of a longitudinal grain, although no

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After the required state of hydrochlorination of the solution is reached, the solution is subjected to steam distillation, until the solvent and the excess hydrochloric acid are driven off. Instead of steam distillation, the solvent and excess hydrochloric acid may be driven off by passing a dry inert gas, such as nitrogen, or air, through the solution. This may be followed by washing the mass with an ammonia solution to remove remnants of hydrochloric acid which forms ammonium chloride with the solution. The residual mass of rubber hydrochloride obtained from the reaction is washed with water to remove remaining traces of hydrogen chloride and the ammonium chloride and the mass is then dried in a vacuum drier.

To make a rubber hydrochloride film, the product so obtained is again dissolved in a suitable solvent, preferably chloroform, to form a 5% solution by weight. Other solvents may be used for this solution, such as dichlorethylene or acetylene tetrachloride. If the product is to be coloured, a suitable soluble dye is added to the solution, and if the product is to be opaque, insoluble colouring ingredients are added to the solution. To this solution is added a small percentage of a protective organic substance, for instance, 3% by weight of cyclohexylamine formaldehyde, to resist the deterioration of the compound under the action of the sun. Other protective organic substances, such as ditetrahydrofurfurylamine, methyleneaminoacetonitrile and cyclohexylamineacetonitrile may be used instead.

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grain may actually be observed in the stretched film.

The treatment of rubber hydrochloride film by a longitudinal stretching process, described above, does not increase its tearing and tensile strength in lateral direction, but the film can be given the desired characteristics in both directions by stretching the heated plastic film laterally, as well as longitudinally. By superimposing several stretched rubber hydrochloride sheets with crosswise grain directions and fusing the so assembled sheets under pressure while heated to a temperature of about 190° F., thin rubber hydrochloride sheet material is obtained having in all directions a multiple of the tensile strength of the original untreated sheets.

By controlling the approach of the film to the heating surface and by varying the character of the heating surface, the appearance and the texture of the final stretched film may be controlled within wide limits. The new process may also be used for obtaining a great variety of lamination products.

To this end a plurality of superimposed untreated rubber hydrochloride films are simultaneously fed over the heating surface and stretched by the stretching rollers, causing the heated plastic films to fuse and coalesce while undergoing the stretching operation and to form, after solidification, a thin homogeneous film having a tensile strength which is a multiple of the tensile strength of a single untreated film.

By varying the heat and adjusting the feed of the sheets just prior to their contact with the heating surface, various longitudinal graining effects are produced in the stretched sheet material. By slightly overlapping the edges of the sheets just prior to the fusing of the material " beaded " edges are formed in the sheet material for improving its appearance and adding to its strength.

By introducing coloured film layers, either above or below or between other film layers, sheet material of an infinite variety of colour ranges and effects is produced. By introducing the coloured layers between the transparent layers, coloured material that ordinarily would " run " is protected by the outer transparent layers of the stretched product against the effects of moisture or other damage. In addition, the new treatment adds lustre that does not exist in the original material.

By interleaving strips of the coloured rubber hydrochloride film material as they are applied lengthwise to one or more layers of clear material, for instance, coloured strips 22 and transparent sheets 21 shown in the drawing, there are produced a great variety of colours, shades and thicknesses of material ranging from narrow ribbon to wide material suitable for shower curtains, raincoats, table covers, umbrella coverings, packing material, wall covering, dress goods, and the like.

By introducing opaque layers under or between one or more coloured or transparent layers, the available colours are intensified and modified. By coalescing more layers of the same colour, deeper shades of the same colour are obtained.

The single figure of the accompanying drawing illustrates how the process of the invention may be carried out in making the improved ornamental sheet material out of untreated rubber hydrochloride sheet material. To make, for instance, an ornamental sheet having two narrow coloured stripes on a transparent background, two wide transparent film strips 21 and two narrow red strips 22 from suitably supported rolls 25 of untreated sheet material are led over guide rolls 26, through an assembly pattern 27, having slits 28 locating the various strips relatively to each other. The properly assembled sheet strips 21 and 22 are then passed through the narrow outlet of a tapered mouth 30 into the gap between the two feed rollers 31 which feed the assembled lamination pattern over the heating surface of a heating cylinder 32 by way of a cooling compartment 34 to the stretching roller 35 which delivers the finished product to the reel 37.

By using a collection of rolls of untreated rubber hydrochloride sheet material of various colours, widths and textures, supported on a rack from which the materials for making up a particular ornamental pattern may be readily selected, and assembling the material by means of a suitable assembly pattern according to the character of the material that is to be produced, products of different patterns may thus be made readily.

The stretching rollers 35 are driven at the required higher speed than the feeding rollers 31 by any suitable driving mechanism. As the assembled laminations of a given pattern passing over the surface of the heating cylinder 32 are heated to a plastic state, the higher speed of the stretching roller stretches the plastic laminations and causes them to fuse into a homogeneous sheet, the thickness of which is only a fraction of the thickness of the untreated sheets which approach from the feeding roller. The heating action exercised by the heating cylinder on the sheet material that is

moving over its surface may be suitably controlled by varying the supply of heating energy and additional heat may be supplied to the upper layers of the passing sheet material by an auxiliary heater 41 which, like the heating cylinder, may be electrically energized and controlled in accordance with the requirements. The heating cylinder 32 is mounted to roll freely as the heated sheet is drawn over its surface and the heating action applied by the roller to the sheet material passing thereover may be additionally controlled by adjusting the angular area of engagement of the sheet material with the heating cylinder. By providing one or more adjustably mounted rollers adjacent the heating cylinder 32, such as idling rollers 42, 43, the engagement of the sheet material with the heating surface may be readily controlled.

The characteristics of final lamination sheet products obtained by the stretching action may be modified by varying the speed of the individual sheets, for instance, by causing the upper of the two stretching rollers 35 to move at a higher or lower speed than the lower stretching roller. This control may be also exercised by making the speed of one of the two feed rollers 31 greater than the other and by correlating the drive of the heating cylinder with the drive of the feeding rollers or the stretching rollers, or both.

By making the surface of the heating cylinder over which the sheet material passes grained or ribbed, the character of the resulting sheet material may be patterned in various ways to produce grained, ribbed, or a variety of other effects. In a similar way, the surface of one or both idling rollers 42, 43 may be shaped and provided with ornamental or other designs for controlling the texture of new sheet material within wide limits to produce a variety of ornamental designs. The character of the sheet material produced by this process may also be controlled by suitably shaping the slots of the assembly pattern 27 or the outlet of the throat 30. Thus, by making the throat opening somewhat narrower than the widest lamination sheets, the edges of the laminations entering the feeding roller 31 are folded, and beads are formed on the stretched sheet product delivered by the stretching rollers 35.

In a similar way, the slits 28 in the assembly pattern may be made narrower than the sheets which are fed through these slits so that the edges of the passing sheets are folded, causing the assembled lamination to have bead or rib-like formations and producing a final stretched sheet product with bead-like or rib-like formations.

The process described above lends itself to the manufacture of a great variety of sheet material products which may be produced in different colour combinations, and with various kinds of ornamentations, the final material having a lustre and a crackly feel and characteristics which make it much superior to the original untreated material.

By the new process, a given quantity of untreated sheet material is converted into a larger quantity of the new stretched sheet material having characteristics which make it much superior to the untreated material.

The new process makes it also possible to produce sheet material having a great variety of colours, shades, thicknesses and widths ranging from narrow ribbons to wide material suitable for a variety of purposes.

By repeating the stretching process described above with material that underwent a previous stretching treatment, or applying a second stretching treatment to a plurality of laminations of previously stretched materials, new sheet materials richer in lustre and of increased crackliness are produced.

Special ornamental effects may be obtained by perforating or imprinting one or more of the intermediate layers of the laminations fed through the feeding rollers 31, so that, on stretching, a final pattern is given to the stretched treated material delivered by the stretching rollers. In making such patterned material, due allowance must be given to the deformation of the pattern incident to the stretching process.

By applying such second tensioning treatment to a lamination of several pretreated sheets assembled with crosswise grain directions, there is obtained a new sheet material that combines uniform tensile strength in all directions with all the other desirable characteristics of the new material described above.

Special ribbed effects may be produced in such laminations by assembling between the sheet laminations narrow strips of the untreated sheet material so that the resulting stretched material produced out of the ribbed lamination has longitudinal ribs which reinforce the material and give it an ornamental effect.

A variety of other shaped bodies may be made by the process of the invention. Thus by using narrow strips of untreated rubber hydrochloride and rolling back and forth the strip as it is moved over a heated surface and stretching it as it moves away from the heated surface, floss, thread, strings, and similar products

resembling natural gut may be produced. Such thread material is a good substitute for natural gut and is suitable for surgical sutures, for musical strings, for stringing racquets, for leaders in angling, for fishing lines and nets, and other uses in which its high tensile strength and waterproof or non-inflammable characteristics are desirable. It has the additional advantage that it does not tangle as readily as ordinary thread. Such thread and gut may be produced in various colours and various finishes from a very smooth surface to a rougher surface, depending on the surface over which it is heated and moved while twisted and rolled.

An ornamental cord of special lustre and light effects may be produced by using several ribbons of stretched heat-treated rubber halide material made in accordance with the present invention and twisting it while being subjected to heat in the manner described above. Strong tying material in many colour combinations with an unusually high lustre is thus obtained.

Alternatively, special ornamental effects may be obtained by twisting a strip of untreated rubber hydrochloride material with a strip of pretreated rubber hydrochloride material while the two are heated and stretched.

Still other products may be obtained by laminating layers of treated rubber hydrochloride with layers of untreated rubber hydrochloride. Thus, by coalescing superimposed layers of stretched and unstretched rubber hydrochloride sheets while they are heated to a plastic state and releasing them from the stretching force in coalesced condition while they are plastic, a crinkly sheet material is obtained. By heating a lamination composed of narrow strips of prestretched rubber hydrochloride material enclosed between two wider strips of unstretched rubber hydrochloride material to a plastic condition and releasing it from the stretching force before it has cooled down, a strip having a crinkled central surface and ruffled edge portions is obtained.

By assembling laminations composed of sheets having crosswise running grains or ornamental patterns and fusing them in a plastic state while heating, a homogeneous lamination is obtained which combines the pattern effects of the component original sheets.

Since the treated rubber hydrohalide material of the invention requires heating to a higher temperature than such untreated material, in order to render it sufficiently plastic for fusing it to another material, but has much greater tensile strength than untreated sheet material, I combine the properties of the two materials by leaving between laminated portions which have been stretched to increase their tensile strength, small portions which are not stretched and thus can serve for heat-sealing when the material is to be used for making sealed packages. Such material is very desirable as a wrapper for cigarette packages or in similar applications. Such stretched sheet material with intermediate unstretched sealing strips may be obtained by reducing the tension applied to the sheet material at predetermined intervals in the heating stretching operation.

Many variations may be made in the processes of the invention described above.

Thus, for instance, the rubber hydrochloride that is to be subjected to the treatment in accordance with the invention may be prepared as follows: Washed pale crepe rubber is broken up in a mill until it is not materially changed in plasticity by further milling. The milled rubber is then formed into a thin sheet and then subjected in a tight container to the action of dry hydrogen chloride gas at atmospheric or higher pressure up to about 8 atmospheres at a temperature of about 180° F. bringing about a penetration of the gas into the rubber and the hydrochlorination of the rubber. This action is continued 12 to 48 hours, depending on the pressure of the gas and the thickness of the sheet, the use of higher pressures and thin sheets enabling faster completion of the reaction. After the reaction is completed, the residual free hydrogen chloride in the solid rubber hydrochloride is permitted to escape from the container and all traces of the hydrogen chloride can be removed by subjecting the remaining mass to vacuum under increased temperature. The resulting mass is then treated in the way described in connection with the reaction produced by the first method.

Alternatively, the reaction may be speeded up by subjecting well-washed pale crepe rubber milled in the way described above to a dry liquid hydrogen chloride at a low temperature and the required high pressure causing the hydrochlorination of the rubber to be effected almost instantaneously and producing a rubber hydrochloride with a content of about 29% chlorine in a very short reaction time of a few minutes.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A shaped body and particularly thin

sheet, thread, or the like, composed essentially of rubber hydrochloride heated to a temperature at which it is plastic, materially stretched in at least one direction and cooled while in the stretched condition to solidification temperature.

2. A thin sheet according to claim 1 and comprising laminations each stretched in at least one direction and united together, the stretching of the various laminations being effected in the same or different directions.

3. A method of improving a shaped body, and particularly sheet, thread or the like, consisting essentially of rubber hydrochloride, characterised in that a rubber hydrochloride material which is solid at room temperature, is heated to an elevated temperature at which it is plastic and is subjected to stretching while plastic until at least one of its dimensions is materially increased, and then is cooled, while in the stretched state, to solidification temperature.

4. A method as claimed in claim 3, characterised in that at least two plies composed essentially of rubber hydrochloride are rendered plastic by heating and are united and stretched while in a plastic state.

5. In a method as claimed in claim 4, the use of plies of different colours.

6. A method as claimed in claims 4 or 5, applied to plies of great length, characterised in that successive portions of the plies are subjected to heating, uniting and stretching in a continuous process.

7. A method as claimed in any of claims 3 to 5, characterised in that the stretching of the heated rubber hydrochloride material is effected in different directions for obtaining upon cooling a solid body exhibiting increased tensile strength in the directions of the stretch.

8. In a method as claimed in any of claims 3 to 7, stretching the rubber hydrochloride material so that at least one of its dimensions is increased at least three times or until its dimensions in two different directions are increased at least two times.

9. A method as claimed in claim 3, characterised in that at least one ply composed essentially of rubber hydrochloride is rendered plastic by heating and stretched while plastic, and then united with at least one other plasticized ply.

10. In a method as claimed in any of the claims 3 to 9, stretching the rubber hydrochloride material at a temperature of the order of 150° F. to 230° F.

11. A shaped body and particularly a thin sheet, thread or the like formed essentially of rubber hydrochloride and produced substantially as hereinbefore described.

12. A method of improving a shaped body and particularly thin sheet, thread or the like formed essentially of rubber hydrochloride, substantially as hereinbefore described.

Dated this 26th day of April, 1937.

REDDIE & GROSE,
Agents for the Applicant,
6, Bream's Buildings, London, E.C.4.

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