PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to the Preparation of Crude Rubber

I, HAROLD GEORGE CRUIKSHANK FAIRWEATHER, of British Nationality, of 65—66, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (a communication from The B. F. Goodrich Company, a corporation of the State of New York, United States of America, of 230, Park Avenue, City, County and State of New York, United States of America), to be as follows:—

This invention relates to the preparation of crude rubber; that is, rubber in a dry form from which rubber goods may subsequently be made.

Practically all of the rubber now used industrially is obtained from plantations of *Hevea Brasiliensis*. In the early days of the rubber plantations it was found that the milky latex obtained by tapping the *Hevea Brasiliensis* tree could be conveniently worked up into solid rubber by diluting the latex, mixing in a small quantity of dilute acetic acid, pouring the acidified latex into a container having the shape of a thin rectangle and setting it aside for a number of hours until a coherent coagulum is formed. The rectangular sheet of coagulum is then passed between a pair of rollers which compacts it and expresses some of the serum (in addition to that which has already exuded during the coagulation). The sheet may then be passed between a pair of helically grooved rollers to impress a ribbed pattern on it and hung up to dry in a smoke house, in which case the product is known as smoked sheets. The sheet may alternatively be passed between further pairs of rollers over which constant streams of wash water trickle, to wash out as much as possible of the serum, the final thin crepey sheet being hung up to dry in a well ventilated shed, in which case the product is known as crepe rubber. In either case a great deal of manual handling is required. The products are extremely variable in essential properties such as plasticity, rate of vulcanization, color and the like. This variability is due in considerable part to variations in serum content and to variations in drying time. The compacted coagulum requires a number of days to dry, in the course of which time bacterial changes in the serum constituents still present in the rubber bring about marked changes in the properties of the product, the magnitude of the changes obviously depending on many factors including the time during which sufficient moisture is present to support bacterial life. Bacterial changes or mold growth reducing the marketability of the product may even occur after the drying has been completed if the product is accidentally moistened or if the weather is very damp, as is frequently the case in the plantation districts. The retained serum is also responsible for the fact that ordinary rubber is capable of absorbing considerable quantities of water.

Despite long-continued intensive research by many very able investigators, and the suggestion of many different ways of preparing crude rubber from latex, no new method has been able to supplant or even to complement permanently the conventional methods outlined above, either because their cost is out of proportion to any advantages which they may have, or because they not only fail to eliminate, but may even accentuate the disadvantages of the conventional methods.

In carrying out the present invention a crude rubber which resists the absorption of water to an unsurpassed degree is prepared by a process which, in a preferred embodiment, involves the flocculation of diluted latex, separation of the flocs by filtration to form a coherent coagulum, heating to a temperature approaching the boiling point of water, exhaustive extraction with water, and drying the coagulum before any compacting pressure is applied. This process can be modified in many ways, as by omission of certain steps, addition of other steps, or changing the character of certain of the steps, as will be pointed out more fully below, but the outstandingly low water absorption which characterizes the products of this invention is not always attained unless the coagulum is heated and exhaustively extracted as out-

[*Price* 1/-]

lined above. These treatments must be applied to the wet coagulum, as treatment of the rubber after drying gives quite different results.

The product so attained is a crude rubber indistinguishable from the highest grade unsmoked plantation rubber in most respects, including nitrogen content and response to the usual vulcanizing agents, as well as resistance to deterioration, and is therefore plainly not " deproteinized rubber ". Nevertheless this new kind of crude rubber exhibits as low a degree of water absorption as " deproteinized rubber " and is therefore admirably adapted for the manufacture of rubber products required to resist moisture, especially insulation for electric wires and cables, as well as water and beverage hose, tank linings, valves, packings and the like. Furthermore, it is sufficiently free from serum constituents not to support growth of molds or other microorganisms, and does not require smoking or any other unusual precautions to prevent spotting, rusting or other blemishes which are so difficult to prevent when usual procedures are followed. It has the additional advantage that it breaks down more quickly upon mastication than the grades of rubber heretofore known and therefore permits a decided saving of time and power in the preparation of the rubber mixes for vulcanization without requiring the addition of expensive, poisonous or otherwise objectionable mastication accelerators.

Among the modifications which may be employed in practicing the invention, the flocculation of the latex may be omitted and the latex may be coagulated in the usual way, but preferably while more dilute than usual and in far thinner sheets, and these sheets either with or without preliminary mangling or equivalent mechanical treatment to express serum therefrom are heated and exhaustively extracted with water as outlined above. Furthermore, it is not essential that the rubber be dried before any compacting pressure is applied, as it may be creped or embossed with the conventional diagonal ribs if it is desired to follow present-day drying practice, but such treatment closes the surface pores of the rubber so that it may require longer to dry than does the rubber prepared in the manner outlined above.

The heat treatment herein specified is believed to involve cooking or heat-insolubilization of certain protein constituents of the latex. Previous attempts to reduce water absorption of rubber by removal of proteins have been quite troublesome to carry out, because the colloidal nature of the protein has made its removal very difficult; and have damaged the rubber either by reason of the drastic treatment required or by depriving the rubber of its natural accelerators of vulcanization and antioxidants. Such removal of proteins is completely avoided by the process of this invention, in which the rubber is separated from the latex serum by coagulation and accordingly occludes the coagulable constituents of the serum.

The nature of the nitrogenous constituents of rubber and of latex is only imperfectly understood, but inasmuch as the nitrogenous materials undoubtedly include proteins they are herein collectively denominated as proteins as a matter of convenience. These proteins appear to constitute in major part the colloidal part of the serum of Hevea latex and to be irreversibly coagulable. While this suggestion is advanced merely by way of explanation of the results obtained and not as a limitation of the invention, it appears probable that the extraordinarily low water absorption of the products of this invention is attributable to the fact that the proteins are insolubilized so that they do not of themselves take up more than minimal amounts of water, combined with the fact that other water-soluble materials are almost completely removed so as to minimize introduction of water by osmotic forces.

In those cases in which heat-insolubilization of the proteins is supplemented by chemical insolubilization, the chemicals may be supplied before or after coagulation. Thus, formalin, tannin or other protein precipitants may be added to the latex. These agents assist in bringing about flocculation of the latex in addition to their effect on the proteins. On the other hand, the freshly coagulated rubber may be soaked in formalin either before or after it is extracted with water but before it is dried. If the insolubilizing agent is of such a character as to leave a water-soluble residue, it should, of course, be added at such a stage that the residue will be extracted along with the naturally occurring water-solubles. Formalin, if free from acid and non-volatile materials, may be applied after the extraction step if desired. Treatment with ammonia or a volatile amine such as methylamine, ethylamine, or diethylamine just before drying also reduces water absorption in some instances.

The extraction may be combined with the heat treatment by employing hot water for extraction, but similar results may be attained by immersing the rubber in hot water for only a long enough time

to insolubilize the proteins and continuing the extraction with water at ordinary temperatures, but it will be found that diffusion of the soluble materials is much slower at the lower temperatures, and longer washing times will consequently be required. It is generally undesirable to heat the latex prior to coagulation, or to coagulate latex of normal or only slightly reduced dry rubber content, possibly because ionizable materials tend to be occluded in the coagulum by such treatments. Satisfactory removal of water-soluble materials can be accomplished by coagulating very dilute latex—of the order of 2% dry rubber content—and removing the serum as far as possible by suction or expression, and soaking in running water at a temperature of not less than 75° C., and preferably 90° C. for ten minutes or more. The exact time required will obviously vary with the condition of the rubber and the nature of the apparatus, as will be evident from the examples below.

In practicing this invention in a preferred embodiment the latex of *Hevea Brasiliensis* is greatly diluted and is acidified until the original latex globules combine to form aggregates or flocks which remain in suspension in the watery liquid without coalescing to a coherent coagulum, the flocks are filtered off and the filter cake is heated while still wet, and then is dried. In a preferred modification the latex is first treated with a soluble sulfide and allowed to stand a few days before it is flocculated. The filtration is preferably carried out continuously to form a continuous sheet of rubber which should be thoroughly washed on the filter with hot water, and continuously dried. If a soft, plastic rubber, which does not require the usual mechanical breakdown before it is used by the rubber manufacturer, is desired, the sheet may be strongly heated after drying is completed.

The latex as it comes from the tree contains between 30 and 40% of rubber in globules so fine that they pass easily through ordinary filters. The latex may be flocculated without dilution, but is then so thick that filtration is difficult and the filtered rubber is difficult to wash. When properly flocculated and diluted, the latex will contain from 1 to 10% of rubber in fine flocks which may be of microscopic size or even of visible size but which do not coalesce immediately, and somewhat resembles buttermilk in appearance. This flocculated latex can be filtered on any ordinarily fine filter medium such as filter paper or cloth, the watery liquid separating with great rapidity and perfectly free from suspended matter, and wash waters will pass through the filtered rubber with equal facility.

The latex, if quite fresh (not more than a few hours from the tree), can be flocculated directly by the addition of a suitable coagulant in a proportion insufficient to produce a solid clot or coagulum, or even by simple dilution and heating, or by a combination of these methods. If the flocculation cannot be carried out so promptly, a preservative will need be added to the latex to prevent undesirable changes in the latex during the time before the flocculating is actually brought about. Certain preservatives induce desirable changes in properties in the product and may be used for that reason regardless of the time factor just mentioned. The length of time during which the latex will remain in a fluent, flocculated condition suitable for filtration will vary somewhat, depending on the origin of the latex as well as the details of the treatment. Fresh latex must be worked up promptly but suitably preserved latex can be brought to a flocculated condition of great stability which persists for hours or days without appreciable change.

The flocculating agent may be any acid or acidic material such as formic, acetic, propionic, butyric, oxalic, lactic, tartaric, citric, benzoic, tannic, hydrochloric, sulfurous, sulfuric, phosphoric or other acids, or even chlorine water, or acidic salts such as sodium bisulphate, monosodium phosphate, potassium acid tartrate, sodium silicofluoride, or salts of polyvalent metals such as magnesium chloride or sulfate, calcium nitrate or acetate, lead acetate, zinc acetate, aluminium sulfate, alum and the like, but it is preferred to use the simple organic acids such as formic or acetic acid since they are inexpensive and easily handled and do not introduce undesirable or difficultly controllable constituents into the rubber. The proportion used will necessarily depend on the previous history and dilution of the latex, but in the absence of polyvalent metal salts will ordinarily be a quantity sufficient to bring the diluted latex to a pH value of about 3.0 to 5.5. At these pH values the flocculated latex, if prepared from fresh latex, will coalesce to a continuous coagulum after a few hours, but can be filtered without difficulty if delays are avoided. The addition of a small quantity of casein solution or other protein to the latex will prolong the period during which it maintains a fluent flocculated condition, but this expedient is not advised when a rubber of low water absorption is required.

If the latex cannot be treated immedi-

ately, a preservative of some kind must be used. Formaldehyde is an excellent preservative, one volume of commercial 40% formalin being capable of preserving two thousand volumes of fresh latex for 24 hours or more, and has the advantage that it tends to insolubilize the proteins in the rubber and thereby assist in minimizing water absorption in the product. Alkalies or alkaline materials such as sodium or potassium hydroxide, sodium carbonate, trisodium phosphate, sodium sulfide, borax, ammonia, hydrazine, amines, and the like are also suitable. Sodium sulfide has the peculiar property of acting in some way on some constituent of the rubber, so that the latex, after standing 4 to 14 days, can be brought to an extremely stable flocculated condition. The rubber obtained by filtering and drying the rubber flocs contains a small quantity of combined sulfur which apparently has its origin in some combination of the sodium sulfide with the protein of the rubber. This crude rubber has a very low rate of water absorption, a high plasticity and rate of breakdown on mastication, and a light color and freedom from odor, although its general properties, including vulcanizing properties and nitrogen content are those of normal plantation rubber.

The preserved latex is flocculated in much the same manner as fresh latex, except that the quantity of acid must be sufficient to neutralize any alkaline preservative which may be present. The latex may be diluted and then acidified or first acidified and then diluted, or, preferably, slightly acidified and then mixed with slightly acidified water. The flocculate prepared from latex containing preservatives is more stable than that prepared from fresh latex and ordinarily remains workable for several hours, that prepared from latex which has been treated with sodium sulfide and allowed to stand a few days before it is flocculated being particularly stable so that it retains a fluent flocculent condition for 24 hours or more.

The flocculated latex may be filtered in any type of filter which does not apply mechanical pressure to the filter cake, an open-top vacuum filter such as chemists use being suitable for small-scale operation but for large scale operation a continuous filter is preferred.

As a specific example of one embodiment of the invention, latex may be worked up into crude rubber of low water-absorptive capacity but high plasticity, normal rate of vulcanization and normal stability, in an apparatus such as that shown diagrammatically in the accompanying drawing. Latex from a bulking tank 1 is drawn into a treating tank 2, which may be one of a series of similar tanks in which the latex can be aged as described below. Sodium sulfide solution from a supply tank 3 is added in a quantity equivalent to twenty grams of crystalline (hydrated) sodium sulfide for each liter of latex, and the mixture is allowed to stand for two to fourteen days. The latex is then diluted with an equal volume of water from the water main 4, and is mixed with a quantity of 2% acetic acid from tank 5 just sufficient to make it acid to litmus. A flocculating tank 6 is charged with a quantity of water twelve times the original volume of the latex and a quantity of dilute acetic acid from tank 5 equivalent to 0.05% acetic acid in the water. The treated latex is then discharged into the weakly acid water in the flocculating tank 6, which causes it to flocculate so that if not stirred the rubber creams rapidly to the surface leaving a clear serum below. This flocculated latex is quite stable; the cream is readily stirred back into the liquid, and no appreciable change occurs over a period of some 24 hours, hence it may be filtered at any convenient time within this period. If a succession of batches is to be worked up, it will be most convenient to transfer the flocculated latex to a feed tank 7 whence it flows through a suitable constant level device 8 into the trough 9 of a continuous rotating drum filter 10. The rubber particles will be deposited on the cylindrical filter surface as a continuous, coherent but extremely pervious coagulum, while the serum is sucked into the interior of the filter drum. The rubber is washed on the filter by a water spray 11, which, because of the extremely pervious character of the deposit, washes serum substances out of the rubber. The continuous sheet of coagulum from the filter is passed into a tank 12 of almost boiling water, through which it is passed in a series of loops so as to remain for about five minutes in the water. The hot water is continuously renewed so that any traces of remaining water soluble serum substances which it may extract will be washed away. The rubber may then pass through a trough 13 containing 20% formalin solution or ½% ammonia, either of which will somewhat improve the moisture resistance of the product. The rubber is then ready to be dried. If care is taken to avoid mechanical pressure which would close the surface pores of the coagulum and trap the moisture within it, the sheet will dry with extraordinary rapidity, a sheet of 0.012 inch dry thickness drying completely in from six to eight minutes at 105° C. in a

forced circulation dryer such as the dryer 14 shown in the drawing, and even a thicker sheet of 0.04 to 0.06 inch thickness drying in four to ten hours at room temperature. If it is desired to avoid the necessity of breaking down the rubber before it is used in the rubber factory, it will be passed through a hot air chamber 15, which may be regulated to produce any desired degree of softness. Thus a sheet 0.01 to 0.02 inch thick heated five to six minutes at 180° C. will be softened to about the same extent as rubber which has been masticated and is ready for mixing. The sheet rubber, either softened or not, as the case may be, may then be packed. This continuous thin sheet is conveniently rolled up on itself to produce a cylindrical package 16, a spray 17 of suitable adhesion-preventing material such as a talc suspension, zinc stearate, a thin coumarone resin solution or the like being applied to prevent adhesion of the convolutions if desired.

The dry rubber if very light colored and translucent, and will not mold or develop other blemishes even when stored in a humid atmosphere. It breaks down rapidy when masticated, and can be handled in the rubber factory in the usual way and mixed with the usual vulcanizing ingredients without change in character or proportions, since it has a normal nitrogen content of about 0.3% and vulcanizes in the same way as present grades of plantation rubber. Its water absorption, however, is far lower than that of ordinary rubber. A convenient measure of rate of water absorption is to immerse dried sheets about 1/16 to 1/8 inch thick in distilled water at 70° C. for twenty hours and determine the increase in weight. The rubber prepared in the manner herein set forth absorbs less than 0.010 gram water per square inch of surface and if carefully prepared may absorb as little as 0.005, whereas standard crepe or smoked sheet rubber gives values in the neighbourhood of 0.020 or higher. Water absorption rates are slightly lower after vulcanization of the rubber, but however tested the rubber of this invention gives absorption values of only one-third to one-fourth or less of those of present standard grades of plantation rubber.

Latex may also be flocked with acid alone if the latex is quite fresh, by diluting it with an equal volume of water and pouring diluted latex into eight times its volume of 0.06% acetic acid solution. After ten to twenty minutes the latex is well flocculated and may be filtered as described above. The filtration should be completed as rapidly as possible since the latex flocculated in the absence of a preservative is not stable and coheres to a solid coagulum after some four hours.

In another modification, latex is coagulated in the manner now customary on the plantations, except that it is first diluted to 2% dry rubber content. If tanks with separator strips are available, the coagulum is formed in sheets, which may be washed in water at 90° C., sheets of coagulum 3/4 inch thick requiring two hours washing to reach minimum water absorption, and requiring less than twenty-four hours at 55° C. to dry to a sheet about 0.04 inch thick. On the other hand, the coagulum may be pressed before washing, in which case it is immaterial whether the latex is coagulated in sheets or in bulk, although sheets offer some convenience in handling. Because of its extremely low rubber content, it is preferred to subject the coagulum to an initial light pressure while covered with a pervious sheet of cloth or the like, to express a large part of the serum and impart a greater strength and coherence to the coagulum without undue distortion, after which it may be mangled in the customary manner to reduce it to firm thin sheets. Such mechanical treatment removes all but a very small proportion of the serum, and a very brief washing—from ten to fifteen minutes in water at 90° C.—suffices to reduce the water absorptive capacity of the rubber to a minimum. The drying time is about the same as that for the unpressed coagulum, for sheets of comparable dry thickness, but the pressed sheets exhibit a slightly lower water absorptive capacity.

It is evident that the invention can be practiced in many ways different from those hereinabove specifically set forth by way of example, without departing from the novel principles of this invention.

Dated this 14th day of April, 1939.

CRUIKSHANK & FAIRWEATHER,
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Agents for the Applicant.

COMPLETE SPECIFICATION

Improvements in or relating to the Preparation of Crude Rubber

I, HAROLD GEORGE CRUIKSHANK FAIRWEATHER, of British Nationality, of 65—66, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (a communication from The B. F. Goodrich Company, a corporation of the

State of New York, United States of America, of 230, Park Avenue, City, County and State of New York, United States of America), 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 the treatment of Hevea latex to obtain crude rubber therefrom having a normal nitrogen content together with low water absorption, from which crude rubber in dry form and rubber goods may subsequently be made.

Practically all of the rubber now used industrially is obtained from plantations of *Hevea Brasiliensis*. In the early days of the rubber plantations it was found that the milky latex obtained by tapping the *Hevea Brasiliensis* tree could be conveniently worked up into solid rubber by diluting the latex, mixing in a small quantity of dilute acetic acid, pouring the acidified latex into a container having the shape of a thin rectangle and setting it aside for a number of hours until a coherent coagulum is formed. The rectangular sheet of coagulum is then passed between a pair of rollers which compacts it and expresses some of the serum (in addition to that which has already exuded during the coagulation). The sheet may then be passed between a pair of helically grooved rollers to impress a ribbed pattern on it and hung up to dry in a smoke house, in which case the product is known as smoked sheets. The sheet may alternatively be passed between further pairs of rollers over which constant streams of wash water trickle, to wash out as much as possible of the serum, the final thin crepey sheet being hung up to dry in a well ventilated shed, in which case the product is known as crepe rubber. In either case a great deal of manual handling is required. The products are extremely variable in essential properties such as plasticity, rate of vulcanization, colour, and the like. This variability is due in considerable part to variations in serum content and to variations in drying time. The compacted coagulum requires a number of days to dry, in the course of which time bacterial changes in the serum constituents still present in the rubber bring about marked changes in the properties of the product, the magnitude of the changes obviously depending on many factors including the time during which sufficient moisture is present to support bacterial life. Bacterial changes or mould growth reducing the marketability of the product may even occur after the drying has been completed if the product is accidentally moistened or if the weather is very damp, as is frequently the case in the plantation districts. The retained serum is also responsible for the fact that ordinary rubber is capable of absorbing considerable quantities of water.

Despite long-continued intensive research by many very able investigators, and the suggestion of many different ways of preparing crude rubber from latex, no new method has been able to supplant or even to complement permanently the conventional methods outlined above, either because their cost is out of proportion to any advantages which they may have, or because they not only fail to eliminate, but may even accentuate the disadvantages of the conventional methods.

In accordance with the invention, a method of treating fresh or substantially fresh Hevea latex is provided, to obtain crude rubber therefrom having a normal nitrogen content together with low water absorption, which method includes coagulating the latex, heating the wet coagulum to a temperature of at least 75° C. to insolubilize protein constituents and separating water soluble components therefrom before drying. The separation of the water soluble components is effected by exhaustive extraction of the coagulum with water. If desired, the Hevea latex, preferably in a state of extreme dilution, can first be treated to flocculate the same, the flocs being separated by filtration to form a wet coagulum. These treatments must be applied to the wet coagulum, as treatment of the rubber after drying gives quite different results.

The product so attained is a crude rubber indistinguishable from the highest grade unsmoked plantation rubber in most respects, including nitrogen content and response to the usual vulcanizing agents, as well as resistance to deterioration, and is therefore plainly not "deproteinized rubber". Nevertheless this new kind of crude rubber exhibits as low a degree of water absorption as "deproteinized rubber" and is therefore admirably adapted for the manufacture of rubber products required to resist moisture, especially insulation for electric wires and cables, as well as water and beverage hose, tank linings, valves, packings and the like. Furthermore, it is sufficiently free from serum constituents not to support growth of molds or other microorganisms, and does not require smoking or any other unusual precautions to prevent spotting, rusting or other blemishes which are so difficult to prevent when usual procedures are followed. It has the additional ad-

vantage that it breaks down more quickly upon mastication than the grades of rubber heretofore known and therefore permits a decided saving of time and power in the preparation of the rubber mixes for vulcanization without requiring the addition of expensive, poisonous or otherwise objectionable mastication accelerators.

In carrying out the invention, flocculation of the latex may be omitted and the latex may be coagulated in the usual way, but preferably while more dilute than usual and in far thinner sheets and these sheets are heated and exhaustively extracted with water as outlined above. It is not essential that the rubber be dried before any compacting pressure is applied, as it may be creped or embossed with the conventional diagonal ribs if it is desired to follow present-day drying practice, but such treatment closes the surface pores of the rubber so that it may require longer to dry than does the rubber prepared in the manner outlined above.

The heat treatment herein specified is believed to involve cooking or heat-insolubilization of certain protein constituents of the latex. Previous attempts to reduce water absorption of rubber by removal of proteins have been quite troublesome to carry out, because the colloidal nature of the protein has made its removal very difficult; and have damaged the rubber either by reason of the drastic treatment required or by depriving the rubber of its natural accelerators of vulcanization and antioxidants. Such removal of proteins is completely avoided by the process of this invention, in which the rubber is separated from the latex serum by coagulation and accordingly occludes the coagulable constituents of the serum.

The nature of the nitrogenous constituents of rubber and of latex is only imperfectly understood, but inasmuch as the nitrogenous materials undoubtedly include proteins they are herein collectively denominated as proteins as a matter of convenience. These proteins appear to constitute in major part the colloidal part of the serum of Hevea latex and to be irreversibly coagulable. While this suggestion is advanced merely by way of explanation of the results obtained and not as a limitation of the invention, it appears probable that the extraordinarily low water absorption of the products of this invention is attributable to the fact that the proteins are insolubilized so that they do not of themselves take up more than minimal amounts of water, combined with the fact that other water-soluble materials are almost completely removed so as to minimize introduction of water by osmotic forces.

It is often possible to bring about supplementary protein insolubilizing by soaking the freshly coagulated latex in formalin, tanin, or other protein insolubilizing agent, before it is extracted with water. Formalin, if free from acid and non-volatile materials, may be applied after the extraction step if desired, or treatment with ammonia or a volatile amine such as methylamine, ethylamine, or diethylamine just before drying also reduces water absorption in some instances.

The extraction may be combined with the heat treatment by employing hot water for extraction, but similar results may be attained by immersing the rubber in hot water for only a long enough time to insolubilize the proteins and continuing the extraction with water at ordinary temperatures, but it will be found that diffusion of the soluble materials is much slower at the lower temperatures, and longer washing times will consequently be required. It is generally undesirable to heat the latex prior to coagulation, or to coagulate latex of normal or only slightly reduced dry rubber content, possibly because ionizable materials tend to be occluded in the coagulum by such treatments. Satisfactory removal of water-soluble materials can be accomplished by coagulating very dilute latex—of the order of 2% dry rubber content—and removing the serum as far as possible by suction or expression, and soaking in running water at a temperature of not less than 75° C., and preferably 90° C. for ten minutes or more. The exact time required will obviously vary with the condition of the rubber and the nature of the apparatus, as will be evident from the examples below.

In practising this invention in a preferred embodiment the fresh or substantially fresh latex of *Hevea Brasiliensis* is greatly diluted and is acidified until the original latex globules combine to form aggregate or flocs which remain in suspension in the watery liquid without coalescing to a coherent coagulum, the flocs are filtered off and the filter cake is heated while still wet. In a preferred modification the latex is first treated with a soluble sulphide and allowed to stand a few days before it is flocculated. The filtration is preferably carried out continuously to form a continuous sheet of rubber which should be thoroughly washed on the filter with hot water, and continuously dried. If a soft, plastic rubber, which does not require the usual mechanical breakdown before it is used by the rubber manufacturer, is desired,

the sheet may be strongly heated after drying is completed.

The latex as it comes from the tree contains between 30 and 40% of rubber in globules so fine that they pass easily through ordinary filters. The latex may be flocculated without dilution, but is then so thick that filtration is difficult and the filtered rubber is difficult to wash. When properly flocculated and diluted, the latex will contain from 1 to 10% of rubber in fine flocks which may be of microscopic size or even of visible size but which do not coalesce immediately, and somewhat resembles buttermilk in appearance. This flocculated latex can be filtered on any ordinarily fine filter medium such as filter paper or cloth, the watery liquid separating with great rapidity and perfectly free from suspended matter, and wash waters will pass through the filtered rubber with equal facility.

The latex, if quite fresh (not more than a few hours from the tree), can be flocculated directly by the addition of a suitable coagulant in a proportion insufficient to produce a solid clot or coagulum, or even by simple dilution and heating, or by a combination of these methods. If the flocculation cannot be carried out so promptly, a preservative will need be added to the latex to prevent undesirable changes in the latex during the time before the flocculating is actually brought about. Certain preservatives induce desirable changes in properties in the product and may be used for that reason regardless of the time factor just mentioned. The length of time during which the latex will remain in a fluent, flocculated condition suitable for filtration will vary somewhat, depending on the origin of the latex as well as the details of the treatment. Fresh latex must be worked up promptly but suitably preserved latex can be brought to a flocculated condition of great stability which persists for hours or days without appreciable change.

The flocculating agent may be any acid or acidic material such as formic, acetic, propionic, butyric, oxalic, lactic, tartaric, citric, benzoic, tannic, hydrochloric, sulphurous, sulphuric, phosphoric or other acids, or even chlorine water, or acidic salts such as sodium bisulphate, monosodium phosphate, potassium acid tartrate, sodium silicofluoride, or salts of polyvalent metals such as magnesium chloride or sulphate, calcium nitrate or acetate, lead acetate, zinc acetate, aluminium sulphate, alum and the like, but it is preferred to use the simple organic acids such as formic or acetic acid since they are inexpensive and easily handled and do not introduce undesirable or difficultly controllable constituents into the rubber. The proportion used will necessarily depend on the previous history and dilution of the latex, but in the absence of polyvalent metal salts will ordinarily be a quantity sufficient to bring the diluted latex to a pH value of about 3.0 to 5.5. At these pH values the flocculated latex, if prepared from fresh latex, will coalesce to a continuous coagulum after a few hours, but can be filtered without difficulty if delays are avoided.

If the latex cannot be treated immediately, a preservative of some kind must be used. Alkalies or alkaline materials such as sodium or potassium hydroxide, sodium carbonate, trisodium phosphate, sodium sulphide, borax, ammonia, hydrazine, amines, and the like are suitable. Sodium sulphide has the peculiar property of acting in some way on some constituent of the rubber so that the latex, after a few days, can be brought to an extremely stable flocculated condition. The rubber obtained by filtering and drying the rubber flocs contains a small quantity of combined sulphur which apparently has its origin in some combination of the sodium sulphide with the protein of the rubber.

The preserved latex is flocculated in much the same manner as fresh latex, except that the quantity of acid must be sufficient to neutralize any alkaline preservative which may be present. The latex may be diluted and then acidified or first acidified and then diluted, or, preferably, slightly acidified and then mixed with slightly acidified water. The flocculate prepared from latex containing preservatives is more stable than that prepared from fresh latex and ordinarily remains workable for several hours, that prepared from latex which has been treated with sodium sulphide and allowed to stand a few days before it is flocculated being particularly stable so that it retains a fluent flocculent condition for 24 hours or more.

The flocculated latex may be filtered in any type of filter which does not apply mechanical pressure to the filter cake, an open-top vacuum filter such as chemists use being suitable for small-scale operation but for large scale operation a continuous filter is preferred.

In order that the method of the invention may be fully understood, one specific example thereof, to obtain crude rubber of low water absorptive capacity, but high plasticity, normal rate of vulcanization and normal stability, will now be described with reference to the apparatus shown diagrammatically in the drawing accompanying the Provisional Specifica-

tion. Latex from a bulking- tank 1 is drawn into a treating tank 2, which may be one of a series of similar tanks in which the latex can be aged as described below. Sodium sulphide solution from a supply tank 3 is added in a quantity equivalent to twenty grams of crystalline (hydrated) sodium sulphide for each litre of latex, and the mixture is allowed to stand for two to fourteen days. The latex is then diluted with an equal volume of water from the water main 4, and is mixed with a quantity of 2% acetic acid from tank 5 just sufficient to make it acid to litmus. A flocculating tank 6 is charged with a quantity of water twelve times the original volume of the latex and a quantity of dilute acetic acid from tank 5 equivalent to 0.05% acetic acid in the water. The treated latex is then discharged into the weakly acid water in the flocculating tank 6, which causes it to flocculate so that if not stirred the rubber creams rapidly to the surface leaving a clear serum below. This flocculated latex is quite stable; the cream is readily stirred back into the liquid, and no appreciable change occurs over a period of some 24 hours, hence it may be filtered at any convenient time within this period. If a succession of batches is to be worked up, it will be most convenient to transfer the flocculated latex to a feed tank 7 whence it flows through a suitable constant level device 8 into the trough 9 of a continuous rotating drum filter 10. The rubber particles will be deposited on the cylindrical filter surface as a continuous, coherent but extremely pervious coagulum, while the serum is sucked into the interior of the filter drum. The rubber is washed on the filter by a hot water spray 11, which, because of the extremely pervious character of the deposit, washes serum substances out of the rubber. The continuous sheet of coagulum from the filter is passed into a tank 12 of almost boiling water, through which it is passed in a series of loops so as to remain for about five minutes in the water. The hot water is continuously renewed so that any traces of remaining water soluble serum substances which it may extract will be washed away. The rubber may then pass through a trough 13 containing 20% formalin solution or ½% ammonia, either of which will somewhat improve the moisture resistance of the product. The rubber is then ready to be dried. If care is taken to avoid mechanical pressure which would close the surface pores of the coagulum and trap the moisture within it, the sheet will dry with extraordinary rapidity, a sheet of 0.012 inch dry thickness drying completely in from six to eight minutes at 105° C. in a forced circulation dryer such as the dryer 14 shown in the drawing, and even a thicker sheet of 0.04 to 0.06 inch thickness drying in four to ten hours at room temperature. If it is desired to avoid the necessity of breaking down the rubber before it is used in the rubber factory, it will be passed through a hot air chamber 15, which may be regulated to produce any desired degree of softness. Thus a sheet 0.01 to 0.02 inch thick heated five to six minutes at 180° C. will be softened to about the same extent as rubber which has been masticated and is ready for mixing. The sheet rubber, either softened or not, as the case may be, may then be packed. This continuous thin sheet is conveniently rolled up on itself to produce a cylindrical package 16, a spray 17 of suitable adhesion-preventing material such as a talc suspension, zinc stearate, a thin coumarone resin solution or the like being applied to prevent adhesion of the convolutions if desired.

The dry rubber is very light colored and translucent, and will not mould or develop other blemishes even when stored in a humid atmosphere. It breaks down rapidly when masticated, and can be handled in the rubber factory in the usual way and mixed with the usual vulcanizing ingredients without change in character or proportions, since it has a normal nitrogen content of about 0.3% and vulcanizes in the same way as present grades of plantation rubber. Its water absorption, however, is far lower than that of ordinary rubber. A convenient measure of rate of water absorption is to immerse dried sheets about 1/16 to 1/8 inch thick in distilled water at 70° C. for twenty hours and determine the increase in weight. The rubber prepared in the manner herein set forth absorbs less than 0.010 gram water per square inch of surface and if carefully prepared may absorb as little as 0.005, whereas standard crepe or smoked sheet rubber gives values in the neighbourhood of 0.020 or higher. Water absorption rates are slightly lower after vulcanization of the rubber, but however tested the rubber of this invention gives absorption values of only one-third to one-fourth or less of those of present standard grades of plantation rubber.

Latex may also be flocked with acid alone if the latex is quite fresh, by diluting it with an equal volume of water and pouring diluted latex into eight times its volume of 0.06% acetic acid solution. After ten to twenty minutes the latex is well flocculated and may be filtered as described above. The filtration should be completed as rapidly as pos-

sible since the latex flocculated in the absence of a preservative is not stable and coheres to a solid coagulum after some four hours.

In another modification, latex is coagulated in the manner now customary on the plantations, except that it is first diluted to 2% dry rubber content. If tanks with separator strips are available, the coagulum is formed in sheets, which may be washed in water at 90° C., sheets of coagulum 3/4 inch thick requiring two hours washing to reach minimum water absorption, and requiring less than twenty-four hours at 55° C. to dry to a sheet about 0.04 inch thick. On the other hand, the coagulum may be pressed before washing, in which case it is immaterial whether the latex is coagulated in sheets or in bulk, although sheets offer some convenience in handling. Because of its extremely low rubber content, it is preferred to subject the coagulum to an initial light pressure while covered with a pervious sheet of cloth or the like, to express a large part of the serum and impart a greater strength and coherence to the coagulum without undue distortion, after which it may be mangled in the customary manner to reduce it to firm thin sheets. Such mechanical treatment removes all but a very small proportion of the serum, and a very brief washing—from ten to fifteen minutes in water at 90° C.—suffices to reduce the water absorptive capacity of the rubber to a minimum. The drying time is about the same as that for the unpressed coagulum, for sheets of comparable dry thickness, but the pressed sheets exhibit a slightly lower water absorptive capacity.

We are aware of Specification No. 116,324 which discloses a process of drying coagulated or uncoagulated latex by insolubilizing the nitrogenous matter contained therein by the action of heat and then submitting the mass to vacuum evaporation. The object of this procedure is to produce whole latex rubber (containing all the solid constituents of the original latex). There is no disclosure of washing out of water soluble constituents. The product obtained, while very desirable for some purposes, has a capacity for absorbing water even greater than standard grades of crude rubber. The product of the present invention, on the other hand, has greatly reduced water absorption and does not contain water-soluble constituents which are retained in the product of the Specification No. 116,324.

We are also aware of Specification No. 348,101, which discloses a method of making rubber articles by forming directly from an aqueous dispersion of rubber a rubber article substantially in its final shape, washing the freshly formed article with water and drying and vulcanizing the article. The disclosure is essentially directed to the manufacture of rubber articles from preserved latex rather than preparation of crude rubber from fresh or substantially fresh latex; it could not have been foreseen from the disclosure of Specification No. 348,101 that crude rubber of low-water absorption could be prepared by heat insolubilization and thorough washing of a wet coagulum obtained from fresh latex. Specification No. 348,101 points out that the effect of washing the formed article with hot water is to hydrolize and remove water-soluble materials, this being usually possible for materials already partly hydrolized by prolonged contact with ammonia used as a preservative for the latex, but not for the proteins in their original heat-coagulable condition. The fact that preserved rubber latex is quite different from fresh latex has long been known. Practical workers in the rubber industry have consequently understood that processes for working up fresh latex into crude rubber cannot be compared with processes for working up preserved latex into finished rubber articles.

The scope of the present invention is limited to "fresh or substantially fresh Hevea latex". By this term is meant fresh latex either with or without preservatives utilized immediately the same is collected from the rubber tree, or substantially fresh latex containing preservatives which is worked up into crude rubber by the procedure of the present invention after a lapse of not more than a few days, in which interval the preservatives do not bring about any profound changes in the composition of the latex.

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

1. A method of treating fresh or substantially fresh Hevea latex to obtain crude rubber therefrom having a normal nitrogen content together with low water absorption, which includes coagulating the latex, heating the wet coagulum to a temperature of at least 75° C. to insolubilize protein constituents, and separating water-soluble components therefrom before drying.

2. A method according to Claim 1, in which the separation of the water soluble components is effected by exhaustive extraction of the coagulum with water.

3. A method of treating fresh or substantially fresh Hevea latex to obtain

sible since the latex flocculated in the absence of a preservative is not stable and coheres to a solid coagulum after some four hours.

In another modification, latex is coagulated in the manner now customary on the plantations, except that it is first diluted to 2% dry rubber content. If tanks with separator strips are available, the coagulum is formed in sheets, which may be washed in water at 90° C., sheets of coagulum 3/4 inch thick requiring two hours washing to reach minimum water absorption, and requiring less than twenty-four hours at 55° C. to dry to a sheet about 0.04 inch thick. On the other hand, the coagulum may be pressed before washing, in which case it is immaterial whether the latex is coagulated in sheets or in bulk, although sheets offer some convenience in handling. Because of its extremely low rubber content, it is preferred to subject the coagulum to an initial light pressure while covered with a pervious sheet of cloth or the like, to express a large part of the serum and impart a greater strength and coherence to the coagulum without undue distortion, after which it may be mangled in the customary manner to reduce it to firm thin sheets. Such mechanical treatment removes all but a very small proportion of the serum, and a very brief washing—from ten to fifteen minutes in water at 90° C.—suffices to reduce the water absorptive capacity of the rubber to a minimum. The drying time is about the same as that for the unpressed coagulum, for sheets of comparable dry thickness, but the pressed sheets exhibit a slightly lower water absorptive capacity.

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1. A method of treating fresh or substantially fresh Hevea latex to obtain crude rubber therefrom having a normal nitrogen content together with low water absorption, which includes coagulating the latex, heating the wet coagulum to a temperature of at least 75° C. to insolubilize protein constituents, and separating water-soluble components therefrom before drying.

2. A method according to Claim 1, in which the separation of the water soluble components is effected by exhaustive extraction of the coagulum with water.

3. A method of treating fresh or substantially fresh Hevea latex to obtain

crude rubber therefrom having a normal nitrogen content together with low water absorption, which includes coagulating the Hevea latex to produce a solid wet coagulum, while removing the major part of the accompanying serum and thereby separating a considerable portion of the water-soluble components, and then immersing the wet coagulum in running hot water at a temperature of at least 75° C. and preferably about 90° C. to insolubilize protein constituents and separate the remainder of the water-soluble constituents before drying.

4. A method according to Claim 3, in which the wet coagulum is subjected to supplementary protein insolubilizing by a chemical protein precipitant.

5. A method according to Claim 3, in which the wet coagulum is formed into thin sheets before immersion in said running hot water.

6. A method according to any of the preceding Claims in which the Hevea latex, preferably in a state of extreme dilution, is first treated to flocculate the same, the flocs being separated by filtration to form the solid wet coagulum.

7. A method according to Claim 6, which includes adding sodium sulphide to the Hevea latex and ageing for a few days and diluting to about 1 to 10% rubber before flocculating.

8. A method according to Claim 6, which is carried out as a continuous process, said coagulum being removed from the filter as a continuous sheet which is continuously subjected to the further treatment.

9. A method according to any of the preceding Claims, which includes drying the treated coagulum and if desired subsequently softening the same by heating.

10. Crude rubber whenever prepared by the method in accordance with any of the preceding Claims, having a normal nitrogen content of about 0.3% but a water absorptive capacity which is only a fraction of that of standard crepe or smoked sheet rubber.

11. Crude rubber whenever prepared by the method according to any of the preceding Claims, having a normal nitrogen content of about 0.3% but which absorbs not over 0.01 gram water per square inch surface when immersed in distilled water at 70° C. for twenty hours.

12. A method of treating fresh or substantially fresh Hevea latex to obtain crude rubber therefrom substantially as hereinbefore described.

13. Crude rubber whenever prepared by the methods substantially as hereinbefore described.

Dated this 27th day of March, 1940.

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