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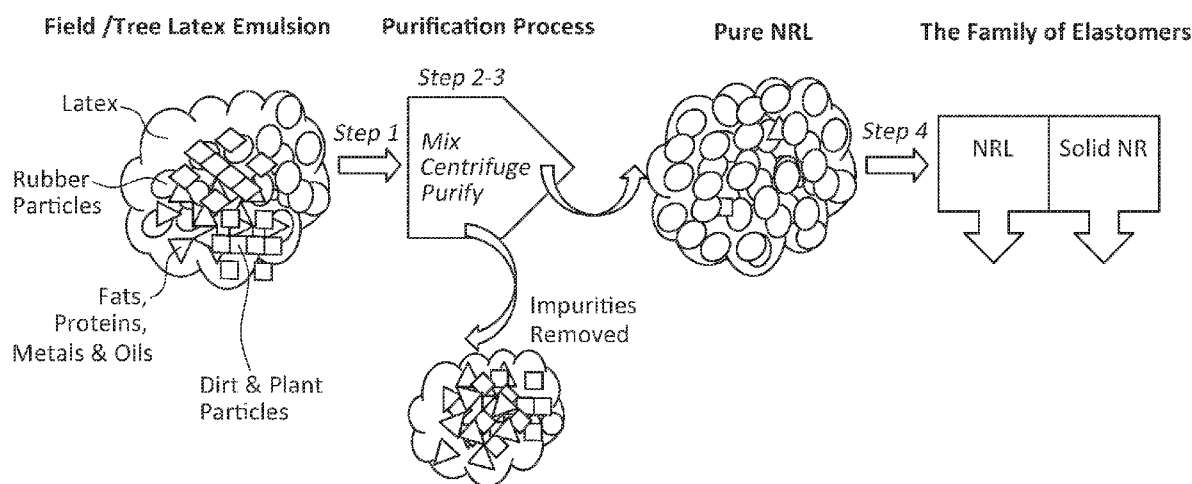


FIG. 3

(57) Abstract: The present disclosure relates to methods for production of deproteinized or purified natural rubber latex from commercially available crude natural rubber latex that has not been purified or partially purified (low-protein), specifically, the present disclosure describes a novel clean in process (CIP) system for purifying natural rubber latex that significantly increases operational efficiency of purification centrifugation run times without stoppage and cleaning, creating a system capable of scale-up. A high-performance purified natural rubber compositions is also described whereby the purified natural rubber has substantially improved softness (modulus) while having increased strength (tensile strength).

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METHODS FOR MAKING PURIFIED NATURAL RUBBER AND COMPOSITIONS

RELATED APPLICATIONS

[1] This Patent Convention Treaty (PCT) International Application claims priority under
5 35 U.S.C. § 119(e) to U.S. Provisional Patent Application Number 63/047,507 entitled,
METHODS FOR MAKING PURIFIED NATURAL RUBBER, filed, July 2, 2020. The
disclosure of the above-listed priority application is expressly incorporated herein by
reference in its entirety for all purposes.

FIELD

10 [2] The present invention relates to a deproteinized or purified natural rubber,
specifically, high performance purified natural rubber having improved physical properties,
specifically greater softness and strength, over commercially available natural rubber source
material or feedstock and methods of producing the same.

BACKGROUND

15 [3] Hevea rubber tapping, collection, processing and production have remained the same
for decades. Typically, natural rubber is extracted from the tree by tapping and collecting
small amounts of liquid natural rubber, which is a polymeric compound of isoprene, i.e.
polyisoprene (C₅H₈)_n with impurities such as other organic compounds including dirt. The
purified natural rubber, methods, and processes provided herein remove the impurities,
20 soluble proteins and unwanted materials, while retaining and concentrating the polyisoprene
protein content.

[4] Hence, the major advantage of the described herein invention, which has not been
previously described or made commercially available, resides in the ability to disassociate
and remove impurities, soluble proteins and unwanted materials from a natural rubber latex
25 or crude feedstock while retaining and concentrating the target rubber component giving rise
to a purified natural rubber that is greater than from about 90% to about 99% free of proteins
as compared to unpurified natural rubber, crude natural rubber or centrifuged natural rubber.
Further, the instant application provides for a purified natural rubber (PNR) and methods for
making such that results in exceptionally consistent, uniform and unambiguous physical
30 properties.

[5] As described in the Detailed Description, the application describes for the first time
purification or ultra-purification natural rubber (solid and latex) composition and methods for
making the same thereof.

SUMMARY

[6] The terms “invention,” “the invention,” “this invention” and “the present invention,” as used herein, are intended to refer broadly to all of the subject matter of this patent application and the claims below. Statements containing these terms should be understood not to limit the subject matter described herein or to limit the meaning or scope of the patent claims below. Covered embodiments of the invention are defined by the claims, not this summary.

[7] A purified, or substantially purified, deproteinized natural rubber emulsion comprising less than about 50 ug/g of total protein.

[8] The purified, or substantially purified, deproteinized natural rubber as in the above, wherein the purified, or substantially purified, deproteinized natural rubber tensile strength is at least 15% greater as compared to unpurified or low-protein natural rubber.

[9] The purified, or substantially purified, deproteinized natural rubber as in the above, wherein the purified, or substantially purified, deproteinized natural rubber green strength is about 60% greater as compared to unpurified or low-protein natural rubber.

[10] The purified, or substantially purified, deproteinized natural rubber as in the above, wherein the purified deproteinized natural rubber softness (Modulus) is about 45% less than unpurified or low-protein natural rubber.

[11] The purified, or substantially purified, deproteinized natural rubber as in the above, wherein the purified deproteinized natural rubber has increased tensile strength and softness as compared to undeproteinized or low-protein natural rubber.

[12] A method for producing purified, or substantially purified, natural rubber substantially free of proteins, the method comprising:

- a. purifying, or substantially purifying, field or centrifuge rubber tree latex in a high speed centrifuge comprising at least a dilution liquid with the latex mixture in a ratio of 1:1 to 1:17, wherein the liquid dilution comprises an anionic high solubilizing surfactant and an alkaline inorganic compound, wherein the mixture extracts non-rubber particles comprising proteins from the rubber particles in the latex; and
- b. purifying, or substantially purifying, the mixture using at least one centrifuge by separating and collecting the rubber particles, wherein the rubber emulsion is about 99% free of soluble proteins, thereby producing a purified natural rubber substantially free of proteins.

[13] A method for producing the purified deproteinized natural rubber as in the above, comprising the steps of:

[14] a) obtaining a batch of rubber tree or low-protein latex; b) Washing the latex in a ratio 1:1 to 1:17 comprising an anionic solubilizing surfactant and an alkaline inorganic compound; c) Centrifuging the composition of step (b), wherein centrifuging the rubber separates the rubber particles from the non-rubber particles; and

[15] d) Collecting the purified deproteinized natural rubber.

[16] The method as in the above, wherein the alkaline inorganic compound is potassium hydroxide (KOH).

[17] The method as in the above, wherein the anionic solubilizing surfactant is a disulfonate.

[18] The method as in the above, wherein the disulfonate is a Sodium Hexadecyl Diphenyl Oxide Disulfonate.

[19] The method as in the above, wherein the non-rubber particles includes proteins, oils, fats, metals, dirt and other non-rubber particles.

[20] The method as in the above, wherein the proteins comprise Type 1 latex allergen proteins.

[21] The method as in the above, wherein the dilution liquid and latex mixture is in on or more containers proximal to the centrifuge.

[22] The method as in the above, wherein the centrifuge is interconnected to the one or more tanks and comprise of one or more control valves or locks and one or more pumps that control the flow of solution to the centrifuge.

[23] Provided herein are scalable methods for producing purified natural rubber substantially free of protein, the method comprising:

- a. Connecting a centrifuge to at least one solution container comprising natural rubber latex and a washing solution, wherein the centrifuge and the containers are interconnected by one or more control valves or pumps to control the flow rate of the solution container to the centrifuge;
- b. Opening at least one control valve to flow the solution to the centrifuge, wherein the flow is at a rate of about 1 to 10 gallons per minute (gpm);
- c. Centrifuging the solution to separate the rubber and non-rubber particles comprising the proteins and collecting the rubber particles; and

- d. Cleaning the centrifuge while continuously and simultaneously separating the rubber and non-rubber particles,
- e. thereby scaling production run time for producing purified natural rubber.

[24] The method as in the above, wherein the method is modular and 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or more centrifuges are interconnected to one or more solution containers.

[25] The method as in the above, wherein the method further comprises one or more pumps interconnected to the centrifuge or one or more containers.

[26] The method as in the above, wherein the centrifuge is cleaned and the wash expelled and collected, thereby extending the operation run times.

[27] A deproteinized natural rubber substantially 99% free of rubber proteins.

[28] The deproteinized natural rubber as in the above, wherein the rubber is a solid or a latex emulsion.

[29] The deproteinized natural rubber of as in the above, wherein the concentration of protein is between about 10 ug/g to about 1900 ug/g, or is less than about 1900 ug/g.

[30] The deproteinized natural rubber as in the above, wherein the concentration of protein is between about 10 ug/g to about 100 ug/g, or is less than about 100 ug/g.

[31] The deproteinized natural rubber as in the above, wherein the concentration of protein is about 50 ug/g.

[32] The deproteinized natural rubber as in the above, wherein the tensile strength and modulus are increased as compared to proteinized or low proteinized rubber.

[33] The deproteinized natural rubber as in the above, wherein the rubber tensile strength is between about 30 MPa to about 40 MPa, or is greater than about 30 MPa.

[34] The deproteinized natural rubber as in the above, wherein the rubber maintains a pot life greater than 2 weeks.

[35] The deproteinized natural rubber as in the above, wherein the rubber maintains a pot life greater than 3 weeks.

[36] The deproteinized natural rubber as in the above, wherein the rubber maintains an alkaline pH stability for 3 weeks or more.

[37] The deproteinized natural rubber as in the above, wherein the rubber maintains an alkaline pH stability for 5 weeks or more.

[38] The deproteinized natural rubber as in the above, wherein the total solid content (TSC) in the rubber is between about 50% to about 65%, or the total solid content (TSC) in the rubber is greater or more than about 50%.

[39] The deproteinized natural rubber as in the above, wherein the rubber has greater green strength as compared to proteinized rubber.

[40] The deproteinized natural rubber as in the above, wherein the rubber is substantially odorless and colorless.

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BRIEF DESCRIPTION OF THE DRAWINGS

[41] The accompanying drawings are included to provide a further understanding of the disclosure and are incorporated in and constitute a part of this specification, illustrate embodiments, and together with the description serve to explain the principles of the disclosure.

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[42] Figure 1 is a diagram describing typical natural rubber tree (e.g. *Hevea brasiliensis*) latex emulsion and/or solid production.

[43] Figure 2 is a diagram describing the 4 principle steps of the purifying natural rubber latex of the present disclosure including obtaining the field latex and treating it with an anionic liquid and basic solution (Step 1); purifying the field latex by high speed

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centrifugation (Step 2); separating and collecting the heavy and the light phase (Step 3); and final treatment to produce the purified NR latex and / or solid.

[44] Figure 3 is a schematic diagram describing the four principle steps as described in FIG. 2 and principle components of field latex including rubber particles (light grey ovals), impurities dirt and other plant particles or debris (yellow squares), and other impurities such as fats, proteins, metals & oils (dark grey triangles).

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[45] Figure 4A is images comparing the color and clarity of the purified NRL emulsions (FIG.4A) and solid NR (FIG.4B) of the present disclosure as compared to other commercially available NRL and solid NR (ribbed smoked sheets of crude *Hevea*). The purified NRL of the present disclosure is substantially more clear or colorless as compared to the other unpurified NRL. The purified solid NR is also substantially colorless or light yellow tint (or off-white) as compared to the ribbed smoked sheets from unpurified NRL.

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[46] Figure 5 is a diagram showing methods for purifying NRL as described in the present disclosure including methods for diluting the field latex with different volumes of diluting mix (1:1, 6:1 and 12:1) consisting of a basic and surfactant solution.

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[47] Figure 6 is a diagram showing another method for purifying NRL as described in the present disclosure starting with estate, cup lump or traditional dry solid rubber and milling and purifying it to a latex emulsion and optional to a solid.

[48] Figure 7 is a diagram showing methods for scale-up production of purifying natural rubber latex whereby purification is a clean in process (CIP) system, whereby the centrifuge is interconnected by valves and/or locks to various solution and/or holding tanks and/or optionally interconnected to a system of pumps to control the flow rate from the solution to the centrifuge, and whereby the centrifuge bowl and interior can be flushed with a washing or cleaning solution and expelled out of the centrifuge while simultaneously and continually separating the rubber and non-rubber particles (or light and heavy phase) for collection, thus increasing operation run times and reducing labor costs.

[49] Figure 8 is a diagram showing a clean in process (CIP) process whereby the tanks or containers, consisting of the dilution liquid: latex mixture and/or other solutions is fed to the centrifuge via a pump or by gravity feed, whereby the tanks are positioned above the centrifuge to create an effective head pressure (through gravity) delivering the mixture to the centrifuge.

[50] Figure 9 is a chart comparing the levels of protein (ug/g) in the purified or deproteinized natural rubber of the present disclosure (PNR) to the Hevea Crude and low protein (LP-1) NRL. The protein level of the purified NRL of the present disclosure is substantially free of proteins as compared to the Crude and LP-1.

[51] Figure 10 is a chart comparing the tensile strength of purified NRL (Purified NR) with zero, 1.0%, 1.75% and 2.5% impurities incorporated into the final purified NRL.

Incorporation of the impurities substantially reduces the tensile strength of the purified NRL processed.

[52] Figure 11 is a chart comparing the tensile strength of compounded purified NRL (Purified NR) with crude and two different lot samples of low-protein NRL (LP-1 and LP-2). The compounded purified natural rubber (Purified NR) has significantly increase tensile strength over the other NRL.

[53] Figure 12 is a chart comparing the tensile strength of uncompounded purified NRL (YPP) with crude and two different lot samples of low-protein NRL (LP-1 and LP-2). The uncompounded purified natural rubber (Purified NR) has substantially increased tensile strength over the other NRL.

[54] Figure 13 is a chart comparing the elongation property of purified NRL (Purified NR) with zero, 1.0%, 1.75% and 2.5% impurities incorporated into the final purified NRL. Incorporation of the impurities reduces the tensile strength of all NRL but does not appear to change the elongation after more than 1% impurities is incorporated.

[55] Figure 14 is a chart comparing the elongation property of compounded purified NRL (YPP) with crude and two different lot samples of low-protein NRL (LP-1 and LP-2). The compounded purified natural rubber (Purified NR) has significantly increased elongation over the other NRL.

5 [56] Figure 15 is a chart comparing the modulus of compounded purified NRL (Purified NR) with crude and two different lot samples of low-protein NRL (LP-1 and LP-2), labeled one, two, three and four, respectively. The compounded purified natural rubber (YPP, labeled 1) has significantly decreased or lower modulus over the other NRL.

10 [57] Figure 16 is a chart comparing the green strength of purified NR (Purified NR) with crude and two different lot samples of low-protein NRL (LP-1 and LP-2). The green strength of purified NR (Purified NR) is significantly higher than that of the other NR.

[58] Figure 17 is a chart showing the pH or alkaline stability of the purified NRL (circle) as compared to crude Hevea NRL (diamond) over time. Purified NRL has more pH sustainability or stability over time (6 weeks).

15 [59] Figure 18 is a chart comparing operational centrifuge run times (hours) for the purification methodologies of the present disclosure with and without clean in process (CIP) systems. The CIP system purification system substantially increases centrifuge run time over that of systems that do not employ CIP.

20 [60] Figure 19 is a chart comparing centrifuge efficiency over time (hours) for purification methodologies with and without clean in process (CIP) systems. The CIP system purification system substantially increases time efficiency over that of systems that do not employ CIP.

DETAILED DESCRIPTION

DEFINITIONS

25 [61] Before describing the present invention in detail, it is to be understood that this invention is not limited to particularly exemplified systems or process parameters that may, of course, vary. It is also to be understood that the terminology used herein is for describing particular embodiments of the invention only, and is not intended to limit the scope of the invention in any manner.

30 [62] All publications, patents and patent applications cited herein, whether supra or infra, are hereby incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference.

[63] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains and as defined in ISO 1382:2012 which defines standard rubber and vocabulary.

Although a number of methods and materials similar or equivalent to those described herein can be used in the practice of the present invention, the preferred materials and methods are described herein.

[64] As used herein, a weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[65] In the application, effective amounts are generally those amounts listed as the ranges or levels of ingredients in the descriptions, which follow hereto. Unless otherwise stated, all amounts and measurements provided herein is in Parts per Hundred Rubber (PHR) and/or where specifically noted may be identified as a Percentage (percentage) of weight based on 100%.

[66] It must be noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a “surfactant” includes two or more such surfactants.

[67] It is also noted that, the ranges described in the inventions are expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[68] As used herein, “ASTM” or formerly known as “American Society for Testing and Materials” is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services including. ASTM's rubber standards are instrumental in specifying, testing, and assessing the physical, mechanical, and chemical properties of a wide variety of materials and products that are made of rubber and its elastomeric derivatives. Rubber, which can either be synthetically produced or derived from the milky colloidal suspension found in latex-producing plants, exhibit unique properties that render it extensively useful in many applications and products.

These rubber standards allow rubber manufacturers and end-users to examine and evaluate their material or product of concern to ensure quality and acceptability towards safe utilization.

[69] As used herein, the term “antigenic protein,” refers to a protein that can induce the generation of antibodies and can cause an immune response in a subject who meets the antigenic protein.

[70] As used herein, the term “biodegradable” as used herein is meant to mean microbial degradation of carbon containing materials.

[71] As used herein, the terms “centrifuge latex”, “centrifuge rubber latex” or “centrifuge natural rubber latex” refers to latex, the rubber particles (light phase) of which has been increased by the removal of heavy phase or B and C-sera by centrifugal force. Centrifuge latex is the common form of commercial NR latex. Centrifuge latex consists of about 60% dry rubber content and available commercially in typically two forms, high ammonia latex (e.g. a maximum of about .0.7% of ammonia) and low ammonia latex (e.g. maximum of about 0.3% of ammonia). The purification process described herein purifies centrifuge latex.

[72] As used herein, “CIP” or “Clean in Process” is a purification process system first described herein that is markedly different from prior purification or centrifugation systems published or known. CIP allows the processing equipment (e.g. the centrifuge) to be cleaned or flushed, expelled and collected. The CIP system described herein (FIGs. 7 & 8) is designed expressly for the purpose of extending centrifuge operational periods, and easy capture of the separate light and heavy phases during different purification processing steps. The CIP process is described in detail in Example 1 and FIGs. 7 & 8. The CIP system is modular, and therefore scalable, so that more than one centrifuge can be interconnected to the same or different containers using shared or different control valves or locks.

[73] As used herein, the terms “compounding” or “compounding agent” or “compounding chemistry” or “compounding ingredient” or equivalents a mixture of a rubber or rubbers or other polymer-forming materials with all the ingredients necessary for the finished product, and the agent or ingredient or chemistry is the substance added to a rubber or rubber latex to form a mix.

[74] As used herein, the term “comprising”, which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. In particular, “comprising” is a term of art

used in claim language, which means that the named elements are essential, but other elements may be added and still form a construct within the scope of the claim.

[75] As used herein, the term “coagulum” or “coagulum content” or “sieve residue” or its equivalent refers to the material consisting of pieces of coagulated rubber, flocculated rubber, latex skin and/or foreign matter, retained under the conditions of the test on a stainless-steel wire cloth with an average aperture width of $180\ \mu\text{m} \pm 10\ \mu\text{m}$, complying with ISO 3310-1.

[76] As used herein, the term “consisting essentially of” limits the scope of a claim to the specified materials or steps; or stated in another way, “consisting essentially of” excludes any element, step, or ingredient not specified, for example, steps of the claimed invention.

[77] As used herein, the term “continuous vulcanization” refers to a process for vulcanizing NRL during continuous passage through specially designed energy transfer equipment.

[78] As used herein, the term “crumb” refers to or is a synonym for ground vulcanized rubber.

[79] As used herein, the term “dewatering” refers to a process of removing excess water when centrifuging crude field latex to concentrate rubber content.

[80] As used herein, the term “dimensional stability” refers to a fabric capable of retaining its original dimensions or shape of the fabric while being used for its required purposes (e.g., dyeing, finishing, washing or any other processes).

[81] As used herein, the term “dry rubber content” or “DRC” refers to the mass in grams of rubber present in 100 g of latex. The percentage of mass of latex, which is coagulated, e.g. coagulated by a weak acid. Dry rubber content can be determined using various methods by means of the hydrometer known as the ‘Metrolac’, which is an instantaneous method.

Methods for DRC are standard in the art, e.g. ISO 124:2014 specifies methods for the determination of the total solids content of natural rubber field and concentrated lattices and synthetic rubber latex. Accurate percentage of dry rubber content (%DRC) and the percentage total solid content (%TSC) of NRL is important for the export certification of shipments of latex in the producing countries. Dry NR process can be in the form of dried or milled sheets, crepes, crumbles, milled sheets or in the form of solid bales.

[82] As used herein, the term “elasticity” refers to the property of rapid recovery of a material to its approximate original shape and dimensions after substantial deformation by a force and subsequent release of that force.

[83] As used herein, “elastomeric fibers” or “soft fibers” refer to any fiber, whether natural or non-natural, that have the ability to stretch 400% or more and return to their original size including but not limited to spandex, or fibers made from NR or NRL as described herein. IUPAC defines the term “elastomer” as a polymer that displays rubber-like elasticity.

5 [84] As used herein, the term “elongation” refers to the length at breaking point expressed as a percentage of its original length (i.e. length at rest). For example, if a rubber component reaches twice its length before breaking its elongation is 100%. In addition, any of the methods described herein and in Figures 2-19 and Table 5 can be modified adapted to provide for a NRL with a desirable elongation factor.

10 [85] As used herein, the term “feedstock”, “natural rubber feedstock”, “field latex”, “tree latex” or equivalents thereof refer to natural rubber raw material with or without a preservative and prior to concentration or any other processing (either in solid rubber or latex form). Typically, the term feedstock refers to a raw material that has not been compounded or has not been treated with additional chemicals or agents or has not been treated with
15 additional chemicals or agents to produce latex with certain physical properties.

[86] As used herein, the terms “green strength” refers to the resistance of raw or unvulcanized rubber compound to tensile distortion or fracture, and therefore a measure of the ability of the rubber or rubber compound to resist distortion during processing and product fabrication.

20 [87] As used herein, the terms “iodine absorption number”, “iodine number”, “iodine value”, “iodine index” or equivalents thereof refers to a value or number of grams of iodine adsorbed per kilogram of carbon black under specified conditions. ISO 1304 contains a method for the determination of the iodine adsorption number. The property is an indication of the surface area of a carbon black.

25 [88] As used herein, the terms “latex” or “natural rubber latex”, “crude rubber latex” or equivalents thereof refers to an “emulsion” or milky liquid, or non-vulcanized rubber, colloidal aqueous dispersion of a polymeric material that is extracted from any of various rubber producing plants and is the source of natural rubber. Latex is not to be confused with plant sap, which is a separate substance, separately produced, and with separate physical
30 properties and functions. Still, as used herein, the term “latex” refers to any polymer in a water-based liquid or viscous state. That is, the term by itself does not specifically refer to natural rubber latex and such distinction will be understood by its use and context in the present application. Still the terms “emulsion” and “latex” may be used interchangeably as it

relates to natural rubber forms, i.e. natural rubber latex (NRL) and natural rubber emulsions may be used interchangeably.

[89] As used herein, the term “latex compounding” or equivalents thereof refers to the addition of the certain chemicals to obtain certain or optimum physical properties in the finished product including but not limited to for example the chemistries to control the colloidal properties, to lower cost of goods, and/or to make it useable for use with available equipment.

[90] As used herein, the term “natural” means at least 98%, at least 99% or about 100% of the components of the invention are derived from a renewable, plant-based, biological material, for example, NR or NRL.

[91] As used herein, the term “modulus” refers to a measure of stiffness under specified conditions of deformation, e.g. compression modulus or shear modulus, whichever applies.

[92] As used herein, the term “natural product” means that at least 95%, at least 96%, at least 97%, at least 98%, at least 99% of the components of the product are derived from a renewable, plant-based biological material, and/or plant and mineral based materials, for example, NR or NRL.

[93] As used herein, the term “non-rubber” or “non-rubber content” refers to constituents other than the polyisoprene rubber including but not limited to protein, lipids, resin and rubber particle membranes, metals, and dirt and/or plant debris. Therefore, industries demand for rubber with a high dry rubber content (DRC) and with the least percentage of non-rubber content or “non-rubber solids”. Methods described herein provide for a purified NR with high DRC and a low NRS, specifically a very low percentage of total proteins. However, methods described herein also provide for a purified NR with a high DRC and a very low NRS, specifically a very low percentage of dirt and other solids besides proteins. In natural rubber or natural rubber latex emulsion.

[94] Similarly, as used herein, the term “non-rubber content” or “non-rubber impurities” refers to contaminants collected during purified natural rubber collection and production. In particular, non-rubber impurities include those contaminants, microorganisms, proteins, dirt and the like in the NR latex serum. In addition, any of the methods described herein and in Figures 2-19 can be modified adapted to provide for a NRL with a desirable low to very low to de minimus levels of non-rubber impurities. As used herein, the terms “optional” or “optionally” as used herein means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or

circumstance occurs and instances where it does not. For example, the phrase “optionally present” means that the substance at reference may or may not be present, and that the description includes instance wherein the substance is and is not present.

[95] As used herein, “protein content” or “total protein content” refers to the amount of protein in any sample, e.g. amount of total protein detected in the heavy and light phases, or in A, B and/or C latex serum, in thin cast films, in latex products like gloves or condoms, or thicker solid rubber products. Various methods can be used to detect size of proteins or protein macromolecules, identification and quantification of the same including but not limited to methods which rely on absorbance properties of macromolecules (e.g., Warburg-Christian, Lowry Assay, and Bradford Assay); methods which rely on spectrometry where detection of single proteins are possible include high-performance liquid chromatography (HPLC) or liquid chromatography–mass spectrometry (LC/MS); antibody detection methods such as enzyme-linked immuno-absorbent assay (ELISA), which is particularly useful for detecting proteins down to pictograms per milliliter (pg/mL), or protein immune-precipitation technique, or immuno-electrophoresis, or Western blot. ASTM D5712 is a Modified Lowry Standard method and is used to quantify the total extractable protein content of a test article or product. This method is not specific for latex proteins but will determine the total amount of protein from Hevea and other sources that are in the test item or test article (e.g. cast film, glove, etc.). However, extracting proteins from a test article is not efficient, especially if the test article is a thick hard rubber as compared to a thin cast film, or rubber glove; and any of the methods described herein and in Figures 2-19 can be modified adapted to provide for a NRL with a desirable low to very low to de minimus amount of total protein content.

[96] As used herein, the terms “purified natural rubber”, “purified natural rubber latex”, “purified NRL”, “PNRL” or equivalents thereof, is a natural rubber latex that has been compounded to obtain certain physical properties or characteristics of a purified or premium NRL is about 99% protein free (or about 99% deproteinized natural rubber) and may include but is not limited to the following physical properties whereby: i) the total range of protein content is about 50 ug/g to about 200ug/g (see Table 2); ii) the total solids content (TSC) range is between at least 60% (see Table 1), depending on the process parameters and the desired TSC level for the process or requirements for a machine or industry or field; iii) the dry rubber content (DRC) is at least 60% (see Table 1); iv) the non-rubber content (NRC) has a range of about 0.01 to 1.0%, optionally less than 0.5% (see Table 1); v) the pH is a basic pH, for example, the pH is in the range of about 8.0 to 12.0 (see Table 1); vi) the viscosity of

about 60% TSC centipoises (cP) in an uncompounded form ranging from 35 to 100 cP; and a viscosity of about 60% TSC cP in a compounded form ranging from 40 to 200 cP; viii) tensile strength of about 30 to 40 MPa (see Table 3); ix) Green strength of about 30-50 MPa (see Table 4); xi) Elongation percentage greater than 1300% (see Table 5); and xii) Modulus less than 1.3 MPa (very soft, see Table 6).

[97] As used herein, “purified natural rubber” can also be used to describe a deproteinized natural rubber is greater than about 99% free of other non-rubber contents other than protein.

[98] As used herein, the terms “pounds per hundred rubber” or “PHR” means the proportion of a component per 100 pounds of elastomer.

[99] As used herein, the terms “pure natural rubber” or “pure elastomeric natural rubber” are used interchangeably to refer to a process of purifying NR or NRL by removing the non-rubber contents including any contaminants, impurities, non-rubber particle proteins and/or centrifuging and removing the non-rubber B and C-serum of the NR or NRL feedstock.

[100] As used herein, the term “rubber” refers to natural rubber (NR) or synthetic rubber. Rubber has three different definitions, dependent on context: 1) the finished material of a product; 2) the raw material or, 3) an intermediate material used during the manufacture of a product. For customs purposes, “rubber” is defined by the International Harmonized System as meaning “... products, whether or not vulcanized or hard natural rubber, balata, gutta-percha, guayule, chicle and similar natural gums, synthetic rubber, factice derived from oils, and such substances reclaimed”. Rubber is also a family of polymeric materials, which are flexible and elastic. Rubber can be substantially deformed under stress, but recovers quickly to near its original shape when the stress is removed. It is usually made from a mixture of materials (solid or liquid), and in most products the base polymer is cross-linked by either chemical or physical links. Where indicated, the instant application uses “rubber” to principally refer to NR raw material whether in latex or solid form, or rubber particles particularly e.g. dry natural rubber or rubber content. The context of the use of the term will make clear its meaning. Rubber particles consist of a polyisoprene core and a complex membrane composed of lipids and proteins charged negatively at native pH. In context of the methods for purifying NRL described herein, the phospholipid proteins of the rubber particles themselves is not removed during purification, rather it is the soluble protein or protein in the latex serum that is removed. Therefore, for purposes of this invention, the “total protein content” does not refer or include the proteins found in the phospholipids of the rubber particles. Conversely, the “total rubber content” includes all rubber particles with

their phospholipid and protein membranes. Alternatively, in other embodiments, rubber may consist of synthetic latex or synthetic rubber that contains NR or NRL in its formulation. Natural rubbers consist of polymers of the organic compound isoprene or polyisoprene, with minor impurities of other organic compounds, plus water.

5 [101] As used herein, the term “skim rubber” refers to rubber obtained from the dilute latex separated during the concentration of natural rubber latex,

[102] As used herein, the term “sludge” refers to the sediment in uncompounded rubber latex.

[103] As used herein, the term “spandex” or “elastane” are used interchangeably and
10 both mean the same thing and are synthetic polyester-polyurethane copolymer fibers that are known for their elasticity. INVISTA produces LYCRA® brand fiber spandex or elastane.

[104] As used herein, the term “tensile strength” refers to how much force or stress, for example, a rubber material can withstand before breaking. The tensile strength of the rubber is typically expressed as the amount of force in megapascals (10-25 MPa) or pounds
15 per square inch (psi). During this test, we pull the material up to the point of failure. In addition, any of the methods described herein and in Figures 2-19 and Table 3 can be modified adapted to provide for a NRL with a desirable tensile strength value.

[105] As used herein, the terms “tensile modulus” or “tensile stress” refers to tensile stress at a given elongation. As used herein, the term “thermal stability” or “thermal stable”
20 or equivalents thereof refer to any thermal process performed to a fiber or fabric, for example in a steam atmosphere or a dry heat environment and remain its high performance (aka “heat setting”). In addition, any of the methods described herein and in Figures 1 and 4-12 can be modified adapted to provide for a NRL with a desirable thermal stability.

[106] As used herein, the term “total solid content” or “TSC” refers to the
25 percentage of mass of the latex, which is non-volatile at a definite temperature in an open atmosphere and is a measure of the total non-rubber solids in the latex and the measure of the total rubber content.

[107] As used herein, “Type 1 latex allergy” or “immediate-type” or “IgE-mediated latex allergy” or equivalents thereof refers to an immediate upon contact hypersensitivity to
30 natural rubber latex and is an IgE-mediated, or immediate type hypersensitivity reaction to one or more proteins in natural rubber latex. Allergic reactions can occur when there is contact with the skin or a mucous membrane such as the mouth or into the lungs by breathing them in. Hence, as used herein the term “Type 1 latex” are those latex’ whereby the proteins

causing the hypersensitivity have been removed such as the purified elastomeric natural rubber latex (PENRL) described herein with the above physical properties but is not limited to PENRL so long as they meet the high-performance and high purity similar to that described herein for PENRL. That is, Type 1 latex feedstock has been shown not to cause immediate hypersensitivity or IgE-mediated response in those with type 1 latex hypersensitivity.

[108] As used herein, the term “Type IV latex allergy” or “cell-mediate latex allergy” or equivalents thereof refers to a cell-mediate contact dermatitis (type IV) reaction or skin inflammation upon contact or sensitivity to chemicals used to make latex products, rather than to rubber proteins themselves. It is not a life-threatening allergy. It is also possible purified or crude NR (solid or latex) have been shown. Hence, as used herein the term “Type IV latex” are those latex’ whereby certain type IV reaction stimulating chemicals have been added to natural rubber, solid or latex, purified e.g. PENRL, or unpurified.

[109] As used herein, the term “UV stabile” or “UV stabilized” or its equivalent refers to a stabilizer(s) to a polymer or polymer resin to allow it to protect the substance from the long-term degradation from UV light. UV stabilizers work by absorbing or screening out UV radiation and preventing damage. Hence, UV resistant materials by nature resist UV rays and prevent UV degradation. In addition, any of the methods described herein and in Figures 1 and 4-12 can be modified adapted to provide for a NRL with a desirable UV stability.

[110] As used herein, the term “viscous-elasticity” refers to elastomer polymer with both viscosity and elasticity and has very weak intermolecular forces, or low Young's modulus and high failure strain compared with other materials. In addition, any of the methods described herein and in Figures 2-19 can be modified adapted to provide for a NRL with a desirable visco-elasticity property.

[111] As used herein, “vulcanization” refers to a range of processes for hardening rubbers, and “vulcanized rubber” refers to treatment of natural rubber with a vulcanizing agent, including but not limited to elemental sulfur, selenium, tellurium, sulfur compounds, peroxides, quinone compounds, amine compounds, resinous compounds, metal oxides and isocyanates. The most commonly used vulcanizing agents are elemental sulfur and sulfur-containing compounds. As used herein, the term “vulcanization” and “cure” are synonyms and can be used interchangeably.

References

[112] The following references are incorporated by reference in their entireties: US7687602B2 to Sumitomo Rubber Industries Ltd.; JP2002145904A to Kao Corporation & Sumitomo; JP2005015614A to Nagaoka Univ. Of Technology & Toyota;

- 5 WO1996028500A1 to Fuji Latex Company; JP2006307018A to Fumitake Imaizumi; US8476348 to National University Corporation Nagaoka University Of Technology; WO2003082925 to Bridgestone Corporation; JP2004262973 to Bridgestone Corporation; WO2005012365 to Thai Rubber Latex Corporation (Thailand) Public Company Limited; JP2005082766 to Bridgestone Corporation; and JP2006307018 to Fumitake Imaizumi.

10 Methods for purifying natural rubber

- [113] The present disclosure is the first to describe the purification of NRL and provide a commercial product that is substantially free of impurities and proteins (about 99%) while improving certain physical properties (e.g. tensile strength, elongation, modulus) while maintaining similar properties of unpurified or existing NRL (e.g. total solid or rubber
15 content, pH, viscosity). Unpurified NR is a high-performance polymer, so it is uncertain whether the physical properties, which attributes to its high performance, would be maintained or sustained while removing the impurities and proteins.

- [114] Hevea rubber tapping has been unchanged for well over a hundred years. An incision is made in the tree's bark, which cuts through the latex vessels (referred to as "latex
20 expression"), from which the latex product then flows. Natural rubber latex is mainly composed of rubber particles, which core is made of cis-1, 4- polyisoprene and the shell of non-isoprene compounds.

- [115] Timing of the incision must be planned within the planting cycle to optimize the latex yield. Usually ripeness period of a rubber tree is about 6 years. Although they can
25 live to over 100 years, they are typically cut down after about 30 years because tapping over time reduces its productivity of latex or latex expression; and new latex production or expression takes a few days depending upon the condition and health of the tree. The individual rubber tree collection cups are combined into a larger container and then transported to central manufacturing facility where the latex emulsion may be initially filtered
30 and transferred to a storage container or whereby the presence of magnesium (Mg^{2+}) ions, a principle component of NRL destabilization, is removed and then stored. Natural rubber latex or coagulated and dried solid NR is then shipped and used as the starting material or

source material for various industries including tires, which makes up about 70% of the NR demand. See Figure 1.

[116] During the process tree tapping and collecting, ammonia (or other inorganic compound) is usually added as a preservative and stabilizer. Ammonia disrupts the particles of rubber and produces a two-phase product consisting of 30 to 40% solids, which is further concentrated by centrifugation to 60% solids, resulting in ammoniated latex concentrate, which contains 1.6% ammonia by weight (high ammonium NRL) or about 0.15 to 0.25% ammonia (low-ammonia NRL); although low-ammonia NRL requires the addition of a secondary preservative to the latex to avoid coagulation and contamination. Ammonia solutions include low (e.g. 0.2 to 0.3 %) to high (e.g. about 0.7- 0.80% or more) NH₃ w/w of latex and constant amount of mixture between of tetramethylthiuram disulfide (TMTD) and zinc oxide (ZnO) (e.g. in a 1:1 ratio). This said, TMTD is not preferably used in the methods disclosed herein as it converts to nitrosamines, which are carcinogenic. Alternatively, other ammonium compounds can be used to preserve and stabilize the NRL including diammonium phosphate (DAP), ammonium laurate, ammonium molybdate, and ammonium metavanadate. Secondary preservatives may be necessary for low ammonium NRL including sodium pentachlorophenate, tetramethylthiuram disulphide, sodium dimethyldithiocarbamate and zinc oxide.

[117] Hevea rubber tapping, collection and storage has remain unchanged for many decades, the disclosure herein describes various methodologies and improvements to purify the crude or field NRL emulsion or source material, to remove substantially all the impurities in the NRL resulting in a markedly different and improved purified NR (solid and latex) with high-performance physical properties such as those listed in Table 1.

[118] It should be noted that the commercially available centrifuge Hevea NRL emulsion currently available for purchase is distinguished from the purified NR, which is also centrifuged but for a different purpose. Most NRL emulsions are centrifuge because the field latex contains a high water content (high volume) as compared to the total percentage rubber content, so the field latex is centrifuged to concentrate the total rubber (or total solid) reducing the total volume to be shipped. Figure 1 describes generally this standard process used by almost entirely all natural rubber producers worldwide for decades.

[119] The present disclosure describes use of various methods for purifying NR including but not limited to single and/or a plurality of purification/centrifugation steps, chemical agents to improve solubilization and then removal of non-rubber particles or

impurities from the latex, concentrate the rubber content, stabilization methods and agents of the purified NRL emulsion, methods for converting the purified NRL to a solid or the reverse, converting the purified solid NR to an NRL emulsion, long-term storage of intermediate and final purified NRL emulsions, methods for drying and curing purified NR, and methods for collecting additional rubber from waste water during the washing and centrifugation steps. See Figures 2, 3, 5 & 6.

[120] The traditional methods producing commercially available concentrated NRL (such as those mentioned in Table 1 e.g.,) is accomplished exclusively to increase the density of rubber per unit of volume or by weight whereby. This effectively makes cost ratio of mass of rubber per shipping mile more efficient and cost-effective. Field latex contains a rubber content between about 12% to 35% total solid content (TSC). These traditional methods simply remove or dewater the field latex to concentrate the TSC between 45%TSC to 68%. Thus, these traditional methods only reduce the amount of water to reduce the weight and reduce the cost of shipping and in no way, or in a de minimus way, cleans or purifies the NRL as disclosed herein.

[121] Figure 2 describes, for the first time, a process of the present disclosure for purifying natural rubber in 3 to 4 general steps. Step 1: The field latex is mixed with an anionic solution consisting of clean water and at least one inorganic alkali compound and a high soluble surfactant to form a NRL-surfactant wash mixture. Step 2: An electric or pneumatic pump system is used to pump the NRL-surfactant mixture into one or more high-speed centrifuge whilst separating the heavy non-rubber phase components from the light rubber phase components. The heavy phase consists of an B- and C-sera consisting of non-rubber particles including proteins, contaminants and impurities and dirt, whereas the A-sera consists of substantially all rubber (or solid) particles. Step 3: The heavy and light phases are collected in separate containers. Alternative methods are disclosed for capturing residual rubber particles in the heavy phase. The light rubber phase is collected and is substantially free of proteins (99% free) or consists of no more than about 1% protein. Depending on the desired customer use, certain agents are used to concentrate the pure NRL and/or coagulate and cure the purified NRL emulsion to purified solid natural rubber (Step 4). Figure 3 describes graphically Steps 1-4 of the general purification process of NRL. The number or percentage of rubber particles (oval shapes), fats, proteins, metals, oils (triangle shapes), and dirt and plant particles (squares and trapezoid shapes) are just representative of the rubber and

non-rubber components in the NRL emulsion and does not represent actual percentages or ratios of each in any emulsion at any stage.

[122] Figure 4 shows colored images comparing purified NRL of the present disclosure compared to standard crude or centrifuge Hevea or other Hevea low brand NRL (FIG.4A). The improved clarity of the purified NRL over the other commercially available Hevea NRL brands allow for broader use and applications which require white or translucent finished product or those products requiring color. Similarly, the purified solid NR of the present disclosure has improved coloring (light yellow or slight butter color) over existing unpurified solid NR including the ribbed smoked sheet (RSS) solid rubber as seen in FIG.4B. The purified solid NR of the present disclosure becomes once again more translucent when it is processed/milled.

[123] Unlike the traditional methods of concentrating the field latex for shipping as described above, the methods of the present disclosure in addition to ultimately concentrating the NRL, it removes the excess water content in the field latex (dewater) but at the same time certain surfactant and basic mixtures are added to wash impurities and can strip the proteins from the rubber particles (Step 1). The ideal and effective surfactant is one that solubilizes and binds the proteins found on the phospholipid shell surrounding the cis isopropene polymer rubber particles. The proteins become soluble in dilutant solution and high-speed centrifugation separates the protein and impurities into different fractions than the rubber particles (Step 2). In order to facilitate separation of the proteins from the rubber particles, the field latex (or feedstock) is diluted by 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, and 90% (ratios 1:1 up to 12:1, up to 15:1, up to 17:1) using the herein described dilution mixture (see Example 1), including but not limited to potassium hydroxide (KOH) or sodium hydroxide (NaOH), and/or ammonia and a surfactant. An optional surfactant is generally an anionic type that maintains latex stability and solubilizes well with the hydroxide solution. Anionic surfactants should also bind and solubilize the proteins and impurities in the latex emulsion. As such, An optional dilution ratio of 1:1, 2:1, 3:1, 4:1, 5:1, 6:1 and 7:1, and optionally up to 12:1 depending on the dilution liquid may be used to purify and solubilizes the proteins. The purified NRL resulting from the methods disclosed herein may have residual KOH content (at 10% KOH stock solution) ranging between about 0.3% to 1.0% by weight or volume of the purified NRL which is much reduced as compared to commercially available centrifuge latexes with higher levels of ammonia than the equivalent KOH levels disclosed herein. Similarly, the level of anionic

surfactant content in the purified NRL will range between about 0.10% to about 2.5% by weight or volume of purified NRL.

[124] Additionally, various surfactants are available including ionic, anionic and nonionic surfactants, however, after experimenting with several of these surfactants, the methods described herein uses a disulfonate anionic surfactant with a high charge density very stable solution. Suitable anionic surfactants for use herein are all those generally known in the art. In alternative embodiments, the anionic surfactants for use herein include alkyl sulfonates, alkylaryl sulfonates, alkyl sulfates, alkyl alkoxyated sulfates, C 6 -C 20 alkyl alkoxyated. Examples include linear or branched diphenyl oxide disulfonates (DPOS) or mixtures thereof.

[125] In alternative embodiments, such surfactant is a diphenyl oxide disulfonate anionic surfactant, DPOS surfactant molecules have the base structure of alkylated DPO and contain in large part two sulfonate groups; they have excellent association with hydrophobic monomers and would be a good hydrophobic monomer transporter through the water phase to latex particles. In alternative embodiments, DPOS surfactants differentiated by the alkyl group including but not limited to C12 branched, C15 branched, and a C16 linear were tested along with many other anionic surfactants. DPOS offers low foaming (reduces volume load), improved shear stability of the rubber particles and where appropriate in the process, rubber particle selection and redistribution or separation within the colloidal suspension of the finished material product.

[126] The purification centrifugation methods disclosed herein desires a cleaning in place (CIP) system, e.g. FIG. 7 and 8. FIG. 8 describes one such CIP system whereby the tanks, either the process tank or the larger CIP tank consisting of the dilution liquid: latex mixture is fed to the centrifuge via a pump or by gravity feed, whereby the tanks are positioned above the centrifuge as to create effective gravity pressure delivering the mixture to the centrifuge. The pumps can be electronically powered or pneumatic (e.g. positive displacing pump). If not pump is available, FIG.8 shows how the process tank can be elevated above the centrifuge to allow for use pressure attributed to gravity to move or feed the mixture into the centrifuge.

[127] Figure 7 shows a general centrifuge set-up for purifying natural rubber latex described in this disclosure, whereby purification clean in process (CIP) system is adopted that continually flushes out light and heavy phase discharge into different chambers from inside the centrifuges. Alternatively, the CIP system can be adopted with various valves (or

locks) that control the flow (inlets) and expulsion (outlets) of the system. See numbers 1-3 e.g. of FIG.7. These inlets and outlets also allow for continuous monitoring of the pH of the purification to maintain latex stability and adjustment of the pH if necessary accordingly.

This CIP system allows for removed of high solid content cream to be removed from the centrifuge discs and lid to prevent blockage, but also to allow for continuous and longer purification centrifugation run.

[128] The CIP purification centrifugation system disclosed herein provides for a significantly longer run cycle (period of time) than traditional centrifuge methods, from about 1.5X up to 5X longer than centrifugation methods without a CIP system. Similarly, the CIP purification centrifugation system is 10%, 20%, 30%, 40%, 50%, or more efficient at separating the A-, B- and C-sera or the light and heavy phases than centrifugation methods without the CIP system.

[129] In addition, the methods or CIP system disclosed herein allows controllable flow of the dilution liquid and latex mixture to flow into the centrifuge by way of the control inlet valve (FIG.7, no. 2). For example, to ensure the appropriate pressure of the mixture into the centrifuge, the tanks should be at least 10 to about 20 feet above the centrifuge allowing for greater and better control of the mixture flow rate into the centrifuge. See FIG.8.

[130] The present disclosure also describes methods for coagulating purified NRL emulsions to purified solid NR by using various weak acids including but not oxalic acid, sulfurous acid, hydrogen sulfate ion, phosphoric acid, nitrous acid, hydrofluoric acid, methanoic acid, benzoic acid, acetic acid, formic acid and/or citric acid. Those skilled in the art will appreciate that any weak acid may work so long as it incompletely dissociates in water to yield an equilibrium state that contains the weak acid and its ions. For example, hydrofluoric acid (HF) is a weak acid because some HF remains in an aqueous solution, in addition to H^+ and F^- ions. This is a property among all weak acids.

[131] Alternatively, natural solidification or coagulation can also occur by microorganisms present in the NRL or addition of microorganisms to the NRL. In a controlled purification process, the existence of natural found microorganisms in the NRL is not desirable and may lead to early, inadvertent, or unintentional coagulation or maturation of the NRL or such before further processing. In fact, removal of such microorganisms in the NRL is part of the process of purification of NRL described herein. The main genera found in Hevea include but are not limited to Bacillus, Lactococcus, Enterobacter, Serratia, Streptomyces and Micrococcus.

[132] The described methods herein have been performed for guayule shrub (*Parthenium argentatum*) and common rubber tree (*Hevea brasiliensis*), and adaptable for purification of other plant-based rubber (polyisoprene) feedstock including but not limited to rubber fig (*Ficus elastica*), Panama rubber tree (*Castilla elastica*), various spurges (*Euphorbia* spp.), lettuce (*Lactuca species*), the related *Scorzonera tau-saghyz*, various *Taraxacum* species, including common dandelion (*Taraxacum officinale*) and Russian dandelion (*Taraxacum kok-saghyz*).

[133] In summary, the present invention uses a high dilution ratio (volume of added water to the latex) to deproteinize water-soluble proteins ranging from 0.25:1 to 17:1 and utilizes a surfactant to aid in dislodging bound proteins from rubber particles, allowing them to become serum associated and removable by density separation. The presence of the surfactant in the dilution solution assists also in promoting latex stability. Further processing of the purified latex (emulsion) to produce coagulated or dry solid rubber may be carried out by using the general multistage method described in more detail in Examples 1 and 2 including:

[134] 1) Ammonia reduction of the concentrated and purified latex by means of slow agitation and evaporation at material and/or ambient temperatures above 18C;

[135] 2) Dilution of concentrated and purified latex from 45-65% TRC to 10-20% TRC using clean water (deionized water may also be used.);

[136] 3) Diluted latex mixture is placed into coagulation trough of appropriate volumetric capacity;

[137] 4) A weak acid, (acidic, acetic, formic and/or nitric acid and calcium nitrate) is added to the dilute latex mixture and stirred repeatedly to ensure complete incorporation of the acid;

[138] 5) Increased stability allows the latex to remain in large containers for several hours while coagulation;

[139] 6) Once fully coagulated the coagulated rubber is removed from the containers, rinsed with clean water and then either milled into small particle size (to increase surface area and promote drying) or forced through rollers to form thin sheets and allowed to dry by placing in an oven or air dried by hanging the sheets over racks; and

[140] 7) The dried rubber is ready for packaging, shipping and use. When the present invention methods were performed and test articles made from the rubber, the articles

had an average of about 21% increase in elongation, about 19% increase for tensile strength and about 18% reduction in modulus.

Physical Properties of Purified Natural Rubber

[141] The primary purpose for removing proteins or deproteinizing raw or native sources of natural rubber is to limit its potential impact to humans regarding allergic reactions in specific rubber (latex) in products such as gloves, condoms and catheters. Moreover, total proteins found in natural rubber latex, resides in two primary locations: freely dispersed throughout the serum (also known as soluble proteins) and those attached (bound) to the rubber articles (also known as bound proteins). It has been demonstrated that source of sensitization in type I hypersensitivity appears to be the native and water-soluble proteins in the natural latex sap (the raw material or feedstock) and not specifically the proteins bound to the rubber particles.

[142] Tomazic et al. (1995) showed that water-soluble proteins from unprocessed raw latex, raw ammoniated latex, and latex products were extracted with phosphate-buffered saline at room temperature for an hour and antibodies from patients with symptoms to latex allergies were used to perform Western blots to determine the size of latex water-soluble proteins to which they bound and were sensitive to. Variations in levels of the water-soluble proteins were determined among different types of products, as well as among samples of the same type of product obtained from different sources. The amount of extractable proteins varied markedly, not only among various types of products but also among products of the same group (from 0.1 to 5.8 mg/article). The IgE immunoblots using the IgE present in human sera against the raw latex proteins indicates that individual antibody responses are quite diversified, but that most of the sera reacted with major antigenic molecules (45 kd, 35 kd, and 25 kd), with the 45 kd band being predominant. See Vesna J. Tomazic, et al. (1995) Characterization of the allergen(s) in latex protein extracts, *J. of Allergie and Clinical Immunology*, 96 (5): 635-642.

[143] Existing publications describe methods for removing, destroying or blinding of proteins in the natural rubber latex using standard methods of saponification and then subsequently vulcanized and maintaining high-performance natural rubber is not the purpose nor a priority. This is distinguished from the present invention which optimized processes of purifying or deproteinizing feedstock rubber not only to reduce or eliminate the impact of certain proteins for those with Type I allergies, but to also provide a high-performance rubber

that is capable of being used across different industries including but not limited to medical, automobile and outdoor industries.

[144] The purification and testing methods described herein were performed prior to and after purification trials to determine changes in protein levels of the raw source or feedstock latex as compared to the post-purification latex. Surprisingly, in view of prior publications, the deproteinization methods of the present invention produced a high-performance purified (deproteinized) natural rubber composition as compared to the natural rubber composition that has not been deproteinized or even as compared to commercially available natural rubber that is claimed to be “low-protein”, including:

[145] 1) Green strength increased from an average of 5.1/MPa to 8.2/Mpa or about 60% increase over the unpurified or low-protein natural rubber;

[146] 2) Elongation increased from an average of 1,121% using a standard glove compound formula to an average of 1,423% or about 26% increase; and with one optimized formulation achieving 1,552% or about 38% increase over the unpurified or low-protein natural rubber;

[147] 3) Tensile strength increased from an average of 31.46/MPa to an average of 37/MPa or about 18% increase over the unpurified or low-protein natural rubber;

[148] 4) Modulus, an indicator of softness of the rubber, decreased from an average of 3.6/MPa to 1.98/MPa or about 45% decrease over the unpurified or low-protein natural rubber. The lower the Modulus number (MPa) the softer the natural rubber, which is preferred for many medical and consumer applications. Typically reduced Modulus corresponds with decrease strength or tensile strength. It was therefore surprising that the methods of the present invention resulted in a softer purified (deproteinized) natural rubber was actually stronger (tensile strength); and

[149] 5) pH stability was found to become longer based on multi-month testing.

[150] Persons skilled in the art will readily appreciate that various aspects of the present disclosure can be realized by any number of methods and apparatus configured to perform the intended functions.

[151] As used in this specification and the claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise.

[152] Unless specifically stated or obvious from context, as used herein, the term “or” is understood to be inclusive and covers both “or” and “and”.

[153] Unless specifically stated or obvious from context, as used herein, the term “about” is understood as within a range of normal tolerance in the art, for example within 2 standard deviations of the mean. About (use of the term “about”) can be understood as within 20%, 19%, 18%, 17%, 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%,
5 4%, 3%, 2%, 1%, 0.5%, 0.1%, 0.05%, or 0.01% of the stated value. Unless otherwise clear from the context, all numerical values provided herein are modified by the term “about.”

[154] Unless specifically stated or obvious from context, as used herein, the terms “substantially all”, “substantially most of”, “substantially all of” or “majority of” encompass at least about 75%, 80%, 85%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99% or
10 99.5%, or more of a referenced amount of a composition.

[155] The entirety of each patent, patent application, publication and document referenced herein hereby is incorporated by reference. Citation of the above patents, patent applications, publications and documents is not an admission that any of the foregoing is pertinent prior art, nor does it constitute any admission as to the contents or date of these
15 publications or documents. Incorporation by reference of these documents, standing alone, should not be construed as an assertion or admission that any portion of the contents of any document is considered to be essential material for satisfying any national or regional statutory disclosure requirement for patent applications. Notwithstanding, the right is reserved for relying upon any of such documents, where appropriate, for providing material
20 deemed essential to the claimed subject matter by an examining authority or court.

[156] Modifications may be made to the foregoing without departing from the basic aspects of the invention. Although the invention has been described in substantial detail with reference to one or more specific embodiments, those of ordinary skill in the art will recognize that changes may be made to the embodiments specifically disclosed in this
25 application, and yet these modifications and improvements are within the scope and spirit of the invention. The invention illustratively described herein suitably may be practiced in the absence of any element(s) not specifically disclosed herein. Thus, for example, in each instance herein any of the terms “comprising”, “consisting essentially of”, and “consisting of” may be replaced with either of the other two terms. Thus, the terms and expressions which
30 have been employed are used as terms of description and not of limitation, equivalents of the features shown and described, or portions thereof, are not excluded, and it is recognized that various modifications are possible within the scope of the invention. Embodiments of the invention are set forth in the following claims.

[157] The invention will be further described with reference to the examples described herein; however, it is to be understood that the invention is not limited to such examples.

EXAMPLES

5 EXAMPLE 1 – METHODS FOR PRODUCTION OF (DEPROTEINIZED) PURIFIED NATURAL RUBBER

[158] Natural rubber is a high-performance polymer and it has been circulated that its desirable physical properties are due to the total sum of its components: Rubber particles consisting of a cis-1, 4-polyisoprene hydrophobic core and surrounded by hydrophilic phospholipid monolayer and impurities including but not limited to oils, fats, proteins, 10 metals, dirt, plant debris, etc. For example, (unpurified) NR has good physical and mechanical properties including tensile strength (500-3500 PSI), elongation (300-900%), adhesion, compression, impact, tear and abrasion resistant, resilience or rebound. Natural rubber has good thermal properties including stable at low (-20° F to -70° F) and high (+180° F to +220° F) temperatures. Still, NR has certain other environmental performance properties 15 that have impeded its use potentially in certain goods that need good color ability, odorless, permeability, sunlight and ozone resistance, radiation resistance, and general weather resistance. In addition, NR has certain Type 1 latex allergens (or proteins) that limit wearables to be made from NR.

[159] However, it is not certain whether removing all or substantially all the proteins 20 from NR would maintain those good physical properties while allowing for other applications such as medical use and devices, direct skin wearables and the like. The present disclosure describes methods for purifying NRL and is intended to remove proteins generally, including those proteins known to cause Type 1 latex allergies. Prior studies purifying NRL to remove proteins had been performed, e.g., Guayule (*Parthenium argentatum*), but on a bench-scale 25 and testing for other physical & mechanical properties were not determined or reported. See Cornish and Brichta (2002), Purification of Hypoallergenic Latex from Guayule, in *Trends in New Crops and New Uses*. J. Janick and A. Whipkey (eds.). ASHS Press, Alexandria, VA. Further, removal of proteins in Guayule, which NR is not yet commercially available, fails to solve Type I IgE-mediated latex allergy triggered by Hevea latex proteins. Nearly 14 million 30 metric tons of NR is produced each year from Hevea. Hence, the present disclosure provides methods for a large-scale production of purified NR that is substantially 99% free of proteins, while maintaining and/or improving the high-performance physical, mechanical and environmental properties of NR.

[160] Proteins in NRL can be separated when subjected to ultracentrifugation at about at high speeds, e.g., over 50,000 relative centrifugal force (or G-force), or about 7300 rpm, the speed of an industry Alfa-Laval disk-stacked centrifuge. At high-speeds, the field latex separates into at least two and / or three main fractions: (1) a top fraction consisting of rubber hydrocarbon particle phase (aka light phase); (2) a middle fraction (or C-serum) consisting of soluble and suspended latex particles; and (3) a denser bottom fraction (or B-serum) consisting of nonrubber particles. Total NR proteins consists of about 1% to 1.5% of commercially available Hevea latex with about a quarter of this being found in the rubber (or light) phase attributed to the embedded or membrane proteins in the phospholipid shell, about half in the heavy or latex or C-serum phase, and about a quarter in the bottom or heaviest B-serum fraction. Natural rubber proteins may be in either the middle or the bottom fraction (C- and/or B-sera). Certain allergen causing proteins include but are not limited to lutoids, Hev b 1, 2, 3, 4, 5, 6, 7 and about 13 other proteins some of which are not well characterized. Methods of the present disclosure remove substantially all of these allergen specific proteins from the final purified NRL.

[161] A study of these proteins revealed that there are two major surface-bound proteins of 14 kDa and 24 kDa in the rubber particle phase. See Hasma H, Amir-Hashim MY (1997) *J Nat Rubber Res* 12:21-32, while the soluble (free not bound) proteins in C-serum ranged from about 7 kDa to as high as 133 kDa, and then those proteins B-serum were about 14 kDa to about 45 kDa. Commercially available Hevea latex emulsion has been centrifuge to concentrate the rubber content, and some of these proteins are removed during this initial centrifugation (see FIG.1). The small fraction of proteins that remain, however, are at least some of the residual extractable proteins (EPs) implicated in Type 1 latex allergy reactions. See Nieto A, Mazón A, Estornell F, Boquete M, Carballada F, Martínez A, et al. (1998) *J Allergy Clin Immunol* 101:S207. Thus, the purification process of NRL described herein is markedly different from other commercially available or known NRL purification methods or commercially available centrifuged latex because it describes for the first time: 1) a pure or ultra-pure NR that has a de minimus amount of protein and should not appreciably cause Type 1 latex; 2) a purified NR that is high-performance and very good or improved physical, environmental and mechanical properties as compared to existing commercially available unpurified and purified NR; and 3) saleable system that can be modified and set up almost anywhere near a rubber plantation or elsewhere for rubber processing.

[162] Generally, the purification process is based on liquid-to-liquid exchange using a purified, pH-modified anionic solution liquid that dilutes and replaces the tree latex's natural plant water. During this exchange the unwanted water-soluble components in the middle and lower B- and C-sera fractions are removed by high speed centrifugation leaving clean rubber particles in the top fraction that are concentrated to form a high solids emulsion. This process removes >90% and up to 99% in both the middle and bottom fractions consisting of the soluble latex protein as well as stripping proteins from the rubber particles. The dilution mixture consisting of at least a surfactant removes the proteins from the rubber particles and solubilizes them in the liquid mixture and subsequently separating them from the rubber particle in a different fraction.

[163] The method disclosed herein is broken down into four general steps as shown in Figures. 2-3 describing the principle steps of the purifying natural rubber latex including obtaining the field latex and treating it with an anionic liquid and basic solution (Step 1); purifying the field latex by high speed centrifugation (Step 2); purification by separating and collecting the heavy and the light phase (Step 3); and final treatment to produce the purified NR latex and / or solid. Below is a detailed description of the aforementioned four steps.

The Clean in Process (CIP) Modular System

[164] The methods herein use reconcentrated or centrifuged latex although field or tree latex can also be used and the methods would be substantially similar and may include an initial centrifugation step to reduce the total volume or vary the number of washes.

[165] Described herein for the first time is a clean in process or "CIP", which was designed with various iterations, evaluated and validated to show that the CIP system: i) extends the operational (centrifuge) run time before stoppage for equipment cleaning e.g.; ii) improved cost & labor efficiency because it can be cleaned in process or cleaned while simultaneously purifying and separating the dilution liquid and latex mixture into rubber and non-rubber particles (or light and heavy phase); iii) the clean in process system provides for quality testing of the process.

[166] A CIP system such as that shown in FIG. 7 and 8 can be modular, with a series of one or more centrifuges in a series like that shown in FIG. 7, optionally 2 or more centrifuges in series, whereby the one or more centrifuges is interconnected to the one or more solution tanks or containers and /or optionally interconnected to one or more pumps. The CIP modular system controls the flow rate of the solution tanks into the centrifuge as well

as cleaning the centrifuge bowl and interior walls while simultaneously purifying the dilution liquid: latex mixture into rubber and non-rubber particles (or light and heavy phase).

[167] Alternatively, the CIP system the connectors between the one or more solution containers and one or more centrifuge may include one or more size exclusion filters. The

5 CIP system can also control flow rate by control of the valves or locks, e.g. the valve or cam lock can be positioned or opened at 50%, 60%, 70%, and 80% (based on the total lumen diameter of the connector or tube). For example, when the container is full, the flow rate may be opened at 50-60% but as the container empties and head pressure decreases, the valve can be positioned or opened at 80% or more.

10 [168] The CIP system can alternatively adapt the one or more centrifuges with one or more inlets and outlets and pumps, to simultaneously separating the rubber and non-rubber particles while cleaning the interior walls and bowl of the centrifuge, expelling the cleaning flush and collecting it, while still collecting the separate rubber and non-rubber particles.

[169] The CIP system increases not only operational efficiencies but time, labor and
15 cost efficiencies because more time is spent purifying the NRL and less time is dedicated to stopping and manually cleaning the centrifuge when the interior walls and bowls fill up with solid content or particles. Further, when the centrifuge interior walls are cleaned and the solid content collected, such can be incorporated into purified NRL thereby increasing the total solid content.

20 [170] The CIP system can employ any number of pumps to flow the mixture to the centrifuge, however, if a pump does not exist or is not cost effective, the one or more tanks can be elevated at least 10-20 feet above the centrifuge and the mixture is fed to the centrifuge by a pressure head pressure created by gravity and elevation above the centrifuge as shown in FIG.8.

25 [171] The steps below are merely descriptive and the methods are not necessarily limited to the steps described.

Step 1 Solubilization:

[172] The dilution liquid mixture preparation uses soft water, or any water, which is predominantly free of metals, chlorine and biological impurities. However, fresh, naturally
30 occurring water may also be utilized but with less efficiency. Depending on the process ratio being used, an appropriate amount (volume or mass) of dilution liquid is produced. For example, if a one to one (1:1) ratio is to be processed, the appropriate amount of dilution liquid is used in this step. Therefore, for each volumetric quantity of latex an equal amount of

process liquid is prepared. For example, if 100 gallons of NRL is to be processed, then mix together 99.36 gallons of soft water, 0.14% of the volume of DPOS surfactant and then followed by 0.5% of a 10% KOH solution.

[173] The KOH solution is prepared by using 50% KOH stock solution and further diluted to a 10% KOH working stock solution, which is then used to control pH and prevent bacterial growth. To produce 10% KOH working stock solution, mix 900 L of soft water and slowly add 100 L of 50% KOH. Potassium hydroxide is a strong base, but any strong or weaker bases can be used to help neutralize the latex particles, which comprise of negatively charged particles. Alternatively, an effective amount of ammonia, a weak base, may be substituted for KOH, or the 10% KOH solution, and the formula adjusted accordingly. Commercially available NRL are often stored as a low or high ammonium mixture and for some NR products the ammonium and its scent is not desirable and such would ideally be removed. The NRL in the dilution solution is mixed for up to an hour, or from about 30 to 60 minutes. Alternatively, if purifying a low or high ammonium commercial Hevea NRL, then ammonia can be used to control the pH and stabilize the latex. However, for a non-ammonia latex only KOH or similar should be used to control pH and microbial activity.

[174] Prior to solubilizing the field or centrifuge latex, prepare stock solutions similar to the stock and working stock KOH solutions above, or ammonia or other basic inorganic compound solution, then add DPOS surfactant and soft water in a clean sufficiently large size tank, making sure all the outlets and locks are closed. For example, the dilution liquid by weight or by volume, e.g. add 0.14% of DPOS solubilizing surfactant, 0.5% of KOH from a 10% KOH working stock solution and the remainder with soft water (or purified water where the mineral content, metal content and chlorine is diminished). For a 1:1 ratio of dilution liquid to latex, and assuming a 2.5 L total volume, the effective amount would 1.25L of the dilution liquid mixture and an equivalent 1.25L of the NR latex. The calculated total solids at time of liquid dilution and latex mixture formation were about 42%. For another batch size of about 20L and assuming 1:1 dilution liquid to NRL again, use about 6.25 L of a 10% KOH, 1.75 L of a DPOS and the remainder up to 10L of soft water. The dilution liquid can be made directly in the processing tank or a separate dilution liquid tank and added to the process tank with the NRL, e.g. about 10L of NRL if assuming a 1:1 ratio. The dilution mixture should be allowed to mix using a motorized mixer or manually for about 15-20 minutes and the pH monitored and controlled to be about 9.5 to 11 pH accordingly. If the dilution liquid is prepared in the process tank, then the latex is added slowly to the tank at a

rate of between 2 to 8/GPM using a transfer electronic or pneumatic pump. If a pump is not available, the latex can be added into the holding tank by means of a gravity feed. The process batch tank should be of appropriate volume by at least 50% greater than the volume being processed. The latex is optionally added to the process tank containing the liquid dilution solution at a rate of about 10 to about 50 L per minute until all the latex is added.

[175] Any process or CIP system tanks should also have outlets and hoses or tubing with control valves or locks and connectable to the centrifuge and other large containers or tanks for easy flow directly to the centrifuge. The hoses or tubing can adapt to be removable (easy for cleaning) and replaceable like PVC hose and at least 1.5 inches in diameter with an optional diameter of 2.5 to 3.0 inches in diameter and fitted with quick release type locks, such as cam locks. If a CIP system tank, any hose or tubing should be connected to a pump system and that connected to the centrifuge as well. Additionally, a CIP tank and/or a process tank as shown in FIG. 8 can hold the dilution liquid and latex mixture, which can then be fed into the centrifuge. See FIG.7 and 8.

[176] Regardless if by pump or by a gravity feed, one or more filters can be added or adapted to the system to initially capture larger particles, e.g. particle sizes of 200-300 microns or more. Filter size is not particularly important; however, large coagulum should be avoided and prevented.

[177] Alternatively, the dilution liquid may be added to the feedstock latex if the feedstock latex is already in a large enough sufficient container for mixing. The feedstock latex does not have to be first de-ammoniated but can be. And some batch runs, a small amount of DPOS or other surfactant may be added hours or days prior to process run to prime latex with higher than normal solid (60% TSC) or protein content (5,000ug/g or more). A range of about 0.10-0.14% bw/bv may be added using anionic types or ionic or non-ionic surfactants if this is the case.

[178] If using a purification system like the clean in process (CIP) process as shown in FIG.7, then an extra amount of dilution liquid may be prepared since the efficiency of using a CIP and with the high-speed centrifugation and separation is a continuous process and can be operated for constantly for a number of days.

[179] Additional tanks or containers with similar outlets and valves or control locks may be useful for washing the process tank or the latex tank for example to ensure maximum rubber particle irretrievability.

[180] The dilution liquid and latex mixture is gently mixed by a mixer blade and motor system at slow speed of about 2 to 20 RPM, optionally 5-10 RPM, for a period of time between 30 minutes to 12 hours. During this dwell period the mixture pH is monitored and adjusted using the effective amount of 10% KOH solution or ammonia to maintain a mixture pH level between 9.5 to 11. This process is called the mixture dwell period". Modifying the pH of this mixture can be done manually by checking periodically the pH of the mixture and controlling it with KOH or ammonia or it can be done automatically using commercially available pH monitors.

Step 2 Centrifugation:

[181] The method disclosed herein can be modular and scalable depending on the batch size, the size of the facility and cost budget constraints. Methods of purification of NRL can be achieved as described using one industry grade centrifuge or a plurality (in series, in-line) of centrifuges can be used. Various industry capacity centrifuges were explored, but finally an Alfa Laval vertical disc-stack centrifuge, in particular manual-cleaning vertical disc-stack centrifuge MAB series, was deemed to best separate the bi-phasic nature of the NRL emulsion into the rubber light phase and the impurities or latex serum in the heavy phase. For example, impurities or solids (down to 0.5microns) are capable of being separated and removed. The solids accumulate in the centrifuge bowl and can be manually scraped off, removed by hand or washed out. Manual-cleaning centrifuges were also preferred over self-cleaning ones because the NR tended to coagulate in self-cleaning centrifuges.

[182] The mixture as described above in Step 1 (solubilized latex solution) is introduced to a centrifuge by a sinusoidal pump or any system that provides adequate head pressure. For example, adequate head pressure is achieved by elevating the process tank whereby the bottom is a minimum of about 10 feet above the centrifuge inlet valve. This produces sufficient pressure to move the mixture via gravity. The process tank outlet flow control valve connects the hose to a filter unit of high flow volume and low volumetric capacity that ensures a limited amount of mixture is residual in the system during flush. For example, one purification system set up is diagramed in FIG.8 showing a clean in process (CIP) process whereby the tanks, either the process tank or the larger CIP tank consisting of the dilution liquid: latex mixture is fed to the centrifuge via a pump or by gravity feed, whereby the tanks are positioned above the centrifuge as to create effective gravity pressure delivering the mixture to the centrifuge.

[183] To improve efficiency and for scale-up purposes, the centrifuge (or centrifuges) is modified by removing the traditional gravity fed bucket and replacing it with a stainless-steel nozzle arrangement with a threaded end which receives the male cam lock fitting. The centrifuge disc stack cover is optionally fitted with CIP spray nozzles. The centrifuge flow control valve is designed in such a way as to allow flow of the mixture to and inside the centrifuge, while in a different position closed this flow and opens the CIP flush flow and in a different position closes both flows. The cover CIP flow is operated by a different valve. All valves maybe constructed to operate manually or automatically by electronic or pneumatic management or a combination. See FIG. 7 for an examples of one such modified disc-stacked centrifuge system.

[184] Various optimizations of the CIP system and centrifuges can be adapted including various automated or semi-automated or manual control systems such as timers and clocks, pH meters or sensors to monitor the alkalinity of the mixtures, automated or manual means for adding e.g. KOH to control the pH, and other chemical or thermal sensors to stream line and scale up the system.

Step 3: Purification by Separation:

[185] In order to preload and balance the centrifuge drive system, the centrifuge disc stack bowl is filled with dilution liquid prior to starting the ramp up of the centrifuge in. The centrifuge bowl is full when liquid runs freely from the light phase discharge port (see FIG. 7). Start the centrifuge and allow the equipment to run up to operating speed. The dilution liquid is used because it is important that a liquid with a stable or controlled pH is used to fill the bowl prior to the dilution liquid and latex mixture is added. The pH level of the liquid should be maintained 9.5 pH or higher to prevent latex shock and coagulation. Any liquid with a similar pH could potentially work, although the anionic surfactant in the dilution liquid helps lubricate the centrifuge disc stack and prevent disc boundary layer adhesion of rubber. Once the centrifuge is at full speed (generally 10 to 15-minute ramp up period), the cam locks or centrifuge flow control valves are opened, preferably to about 50/60% position, and the dilution liquid and NRL mixture flows into the centrifuge bowl assembly. The flow rate is about 4.0/GPM to about 7.0/GPM. Lower flow rates between 1.0/GPM to 4.0/GPM are also acceptable where process production period is less important. Although lower flow rates may increase coagulum or solid rubber buildup. The prefilled bowl will start to flow light phase and heavy phase. Collect all light phase discharge to a collection container or drum placed proximal to discharge port. Other collection methods may be used.

[186] After about 15 minutes, after the centrifuge is flowed with dilution liquid and latex mixture, a sufficient sample of the light phase from the centrifuge light phase outlet is taken and tested for at least pH, but other testing for percentage of total solid content (TSC) can be done as well. For example, pH and TSC can be accomplished various intervals (e.g. 30, 60, 90 minute) during the entire production run (see FIGs. 7 & 8). Samples of the light phase are used to monitor both pH and TSC and notify any necessary changes to pH and/or the flow rate coming from the CIP or process tank. Target pH is about 9-11 and target TSC is about 56 – 60%.

[187] For example, the lower the flow rate (e.g. valves or locks positioned at less than 50%) the higher the solids content of the light phase because the dilution liquid and latex mixture has been allowed to be retained for a longer period of time within the disc stack and bowl assembly. However, reducing the flow rate alone is not always optimum to increase the TSC in the light phase because when the TSC is too high, the purified NRL is less stable and may coagulate, once it is retrieve from the light phase from the centrifuge or coagulates may occur inside the centrifuge discs. Thus, it is important that the anionic surfactant remain in the mixture to maintain stability during centrifugation cycle. Conversely, too high a flow rate (e.g., valves or locks positioned greater than 60 or 70%) may produce a light phase with low TSC and there is sufficient time to separate out all the rubber particles in the light phase. To control the captured light phase flow rate or flow rate generally from the tanks, the diameters can be adapted (decreased for increase flow rate, increased for decrease flow rate). Further, if there is not CIP system with a pump is used, then the dilution liquid and latex mixture feed flow relies on head pressure, and the PSI will diminish as the level in the process tank drops. In this instance, the flow control valve will need to be opened to greater than 50/60% to 80-90% the as pressure reduces and/or the volume drops.

[188] To determine the pressure (PSI, pounds per square inch) at the centrifuge inlet flow control valve (see FIG. 7), take 0.433 multiplied by the height (feet).

[189] The pH testing can occur throughout the light or heavy phase collection period, and adjusted as needed using again KOH or ammonia to maintain a pH range between 9.5 and 11. Care must be used to add the pH modifier slowly and allow for full mixing prior to testing again after each addition. Once the batch tank is empty, it is possible to open additional process tank volumes and continue to operate the centrifuge until the centrifuge bowl is full of impurities. The CIP system provides for a significantly longer run cycle than

traditional centrifuge methods, up to 50% or more long run period than without the CIP system.

[190] Additionally, due to the increased centrifugation runs, accumulation of a latex cream (high solids content) builds up inside the disc stacks and bowl cover lid which needs to be flushed out or it impedes purification or separation of the light and heavy phases (or A-, B- and C-sera). This cream can be expelled at the light phase port of the bowl cover (FIG. 7, labeled no. 1).

[191] For a starting mixture volume of about 2,500 L, and depending on the centrifuge inlet flow control valve's flow position, a run cycle of 2,500 liters (660.43/gal) with a flow rate of 5/GPM (1,134/liters/min) the run cycle will take approximately 2.2/hours and require two (2) CIP tanks equally spaced. The lower the flow rate the longer the run cycle time.

[192] To shut down the batch run, if using a CIP system, continue to run the centrifuge until the process supply tank is empty and all supply hoses and filter element are significantly reduced. Close the process supply tank flow control valve and open the supply line feed CIP valve to flush the materials from the system prior to terminating the operation of the centrifuge. See FIG. 7, label no. 3. Then when the centrifuge is turned off and allowed to come to a complete stop. Alternatively, or in addition to, the electric braking system may be deployed to accomplish this. When the centrifuge has fully stopped, open the bowl cover flush CIP valve and flush materials from the cover disc bowl may be removed for cleaning or swapped with a new, clean disc bowl assembly and restarted. Backup bowl assemblies are required for this swap-operating mode.

[193] Collect all coagulated rubber materials from the centrifuge. Depending on operating requirements, good laboratory practice and quality control, requires that each sample taken to determine pH and/or TSC, should be weighed and test results recorded to aid in efficiency and/or mass balance documentation.

Step 4 Final Production and Coagulation:

[194] About 500 ml or more of the purified NRL is sampled and tested for quality including physical, environmental and mechanical tests well known in the art and as described for ASTM rubber standards. The specific test can be searched and found on the internet at www.astm.org/Standards/rubber-standards.html. For example, ASTM provides testing standards for the final NRL produced, in this instance purified NR, and/or the products made from purified NR such as surgical gloves and the like. Table 1 shows some of

the tests performed on the purified NR made by the methods described in herein including but not limited to TSC, dry rubber content (DRC), non-rubber content, alkalinity (pH), viscosity, sludge, coagulum, mechanical stability such as tensile, elongation, green strength, and module, other physical properties including color and odor, environmental properties including ozone, UV and thermal stability. Other tests may be performed depending on the nature of the rubber product made as well.

[195] Once the purified NRL has been accepted by quality, it is moved to a maturation tank where it is held for a period of between 30 and 60 days prior to shipment. During this period, the pH of the materials is regularly tested and adjusted, as necessary using ammonia and/or KOH; however, other weak or strong base inorganic compounds may work.

[196] To produce a purified solid NR from the purified NRL, the latex used may be used directly from the purification centrifugation or be removed from the maturation tank. In either case, the pH of the purified NRL will need to be reduced e.g., by de-ammoniating and subsequently diluted with soft water. The latex can be tested until the TSC is between 12% to 25% prior to coagulation (or solidification).

[197] Coagulation of the purified NRL consists of a continuous acidic water flume, hot water washing, and volume reduction if necessary and secondary basic washing stage if necessary. The purified NRL is then cured and dehydrated to form a pure solid rubber.

[198] Additionally, an array of propriety additives was blended into the modified Hevea post process to achieve the desired physical properties. For example, electrical insulating rubber gloves used by lineman need to be water resistant; hence improved water resistance is a desirable physical property to be achieved. In this instance, chemical agents were added to achieve a NRL with a physical property of >100 iodine index or iodine value to impart the water resistance. This is one example of how the purification methods described herein can be modified and adapted to obtain certain desired physical properties of customers and/or industrial and/or consumer products.

EXAMPLE 2 – PHYSICAL PROPERTIES OF PURIFIED NATURAL LATEX, TESTING METHODS AND RESULTS

[199] A variety of materials tests have been designed and performed to demonstrate the physical, mechanical, environmental, visual, objective and subjective, differences between the purified NRL of the present disclosure purified substantially as described in Steps 1-4 in Example 1 above, compared to crude Hevea (typically purchased as centrifuged

or concentrated latex) and a commercially available low protein latex (chemically modified). In addition to comparing these NR latexes, the purification process described herein was also applied to the commercially available “low protein” latex to demonstrate that the method can be utilized and applied to any existing NRL emulsion and improve on this source material. A summary of testing is described in more detail below.

[200] The purified natural rubber methodologies above have been developed, tested and validated, methods including attracting, shedding and removal of both free or soluble and bound proteins using solution chemistry, density separation and gravity filtration. In addition to protein content reduction and removal, the purification process extracts other contaminants, and non-rubber materials (dirt, lipids, sugars, minerals, etc.). However, unlike other published methodologies, the methods herein are optimized to yield a purified high-performance natural rubber that has the performance and physical properties of unpurified natural rubber in either latex (emulsion) or dry solid form.

Testing Assays

[201] The Tables and Figures 9-17 are the results from some of the tests described below. Legend for analyzing these Tables and Figures: YPP (is an internal descriptor for the purified NRL of the present disclosure), Crude (crude Hevea NRL), Centrifuge (crude Hevea NRL centrifuge or concentrated), LP (Hevea Low Protein from Vytex), LP-1 and LP-2 (different lots of Hevea Low Protein from Vytex).

[202] Total Solids Content (TSC). This tests the capability of the methods of the present invention to process low solids content latex (dilution) to achieve industry standard at 58-63%TSC. Each of the ten (10) lots processed achieved a range of TSC from 59.8% to 64%TSC. TSC is only a test to determine the total amount of solids present in the liquid (latex). See also Table 1, 2 & 3.

[203] Total percentage of Non-Rubber Content (NRC). This tests the effectiveness of the methods of the present disclosure as compared to commercially available Hevea crude NRL (control) and commercially available low protein NRL to remove non-rubber impurities, remove non-rubber content, organic and inorganic materials including dirt, plant debris, metals and other unwanted materials including proteins, etc... After each lot was processed (n=10), the purified NRL output was tested with a range of 0.01% to 0.09% and an average of 0.05%; for Hevea crude NRL averaged 2.75% (n=10, different lots, 1L from each drum was tested); and the Hevea low protein NRL averaged 2.39% (n=4, different lots, 1L from each drum was tested). See also Table 1, 2 & 3.

[204] Total Rubber Content (TRC). This tests the effectiveness of the methods of the present disclosure to process and achieve a near Zero delta between TSC and NRC being Total Rubber Content or TRC. That is, $TRC = TSC - NRC$ or where total solids equals total rubber and non-rubber equals near zero. Alternatively: $TSC - TRC = NRC$ as a percentage (%) ($TSC - NRC = TRC$). Each of the ten (10) lots was tested for total rubber content prior to the purification process. The average across the ten (10) lots: 62.57% TSC - 2.75% NRC = 59.82% TRC. After purification, the purified NRL averaged 61.87 % TSC - 0.06% NRC = 61.82% TRC. See also Table 1, 2 & 3.

[205] Total Protein Content. This tests the capability of the methods of the present disclosure to process and achieve a near Zero delta between test detection at each resolution end.

Twenty-one (21) lots of commercially available crude Hevea centrifuged NRL were purchased. Each was tested for protein content. Four (4) of the 21 lots purchased were commercially available "Low Protein" NRL (Vytex). Each lot held a retained sample of the latex as received ("received protein"). A total of six (6) liters were retained for testing and comparison purposes. Each lot's protein was tested and recorded. The lots were then processed using the purification methods described herein. With the exception of the Low Protein lots, the average total Protein ranged from a max of 1542 ug/g to a low of 459 ug/g. The Low Protein lots averaged 845 ug/g with a high of 1,035 ug/g. Received total protein ranged from a max of 12,465 ug/g to a min of 4,432 ug/g and an average of 7,107ug/g. After each lot was purified per the methods described herein, they averaged of 138 ug/g with a low of non-detect (<50 ug/g) to a high of 400 ug/g. The range correlates to a range of dilution wash ratios tested which ranged from 1:1 to 17:1 where the dilution increased to a point that dropped TSC to below 8%. Generally, the higher the dilution ratio the greater the total amount of protein removed up to 9/10:1 where no measurable detection was possible, process periods increased and total production system loss elevated. See also FIG.9 and Table 1, 2 and 3.

[206] Dried Latex Color (air-dried, not coagulated). This tests for the clarity and color of the NRL after purification methods as described herein. Visual comparison was made from 1.5mm to 2.5mm thick cast and air-dried NRL. See FIG. 4A comparing purified, crude and low protein NRL that were transparent, off-white & yellow, respectively. Visual comparison demonstrated a significant decrease in typical yellow-ish color. All ten (10) lots crude Hevea NRL purchased and purified as described herein showed near transparent clarity

over crude Hevea and more significantly of the Hevea Low Protein NRL lots/samples. See also FIG.4.

[207] Dried Latex Color (coagulated). This tests the color of the coagulated NRL. There was a markedly different coloring between the purified NRL of the present disclosure as compared to the both the rib smoked sheet (RSS) solid NR and the baled oven dried NR. See also FIG.4B.

[208] Uncompounded Green Strength: Tensile. This tests the overall general physical properties after purification methods as described herein as compared to crude NRL. Four (4) different types of commercially available NRL were tested. All the NRL (purified, crude and Low Protein) was put in a cast film and compared against two (2) commercially available centrifuged high ammonia and a low ammonia NRL, and two (2) different lots of Low Protein NRL. Each type was cast with three 1.5mm films, which were air dried after one (1) hour at 60C. Green strength improved after purification of the NRL as described herein, and averaged 8.1 from a low of 3.2 Mpa. The feedstock used to produce the purified NRL was baseline and found to produce 3.1 Mpa. See also FIG.10, 11 & 12 and Tables 1, 2 & 3.

[209] Commercial "Low Protein" Latex YPP Production. This test was to demonstrate that chemically decreased latex benefits from the purification methods disclosed herein. Four (4) lots of Low Protein NRL were acquired and were from different production numbers. Each of the latexes was then purified by the methods described herein with different dilution ratios of: 9:1 (PDX-32); 14:1 (PDX-48); 5:1 (PDX-17); and 2.5:1 (PDX-09). The protein content at the start and after purification was tested and compared. Protein content at the Start: PDX-32: 655; PDX-17: 459; PDX-48: 1,542; and PDX-09:876. Protein content after purification: PDX-32: <50 Non detect; PDX-17: <50 non detect; PDX-48: 101ug/g; and PDX-09: <50 non detect. See also FIG.10 and Table 1, 2 & 3.

[210] Uncompounded and De-Ammoniated Odor. Random samples of six different commercial NRL were taken, deammoniated and tested for odor by five individuals using a blind test. All six samples were air dried as films at 1.5mm thickness and tested again in a blind using same five individuals. Of the six samples taken one was a purified NRL as purified by the present disclosure at 4:1 ratio. No compounding was used. All six NRL were found to be acceptable in terms of odor being not pungent or offensive. 80% of testers found the purified NRL as being "Without Any Real Odor" compared to the others. The air-dried NRL samples were found to have a robust to acceptable rubber smell where the purified NRL sample was noted by all (100%) as having "No Odor".

[211] Uncompounded pH Stability. Designed a test to compare a two-liter sample of four samples of latex, where two (2) were purified NRL as described herein and two were crude Hevea NRL. The test took place at 22C in the lab with pH sensors in each of the samples tested and adjusted to 10.25. The samples were covered with the pH sensors and allowed to sit for a period where the pH dropped below 9.0. This took fourteen (14) days for the crude Hevea NRL to drop below pH 9 as compared to purified NRL that did not drop below pH 9 until after 18 days and one sample not until 21 days. On average the purified NRL maintained pH stability above pH 9 for about 19.5 days and the crude Hevea NRL averaged 12.5 days. The pH of the NRL is a general indicator of bacterial activity. That is, as pH drops there is greater potential for growth of bacteria and mold/yeast. This growth appears flat for several days and then there was a rapid decrease in pH as growth increase logarithmically. Purity of the latex appears to reduce these pH-changing loads and allows for a longer maintenance of pH without the need for additional ammonia, bactericide or KOH. See all FIG.17.

[212] Compounded Strength: Tensile, Elongation & Modulus. Using a master batch compound generally regarded as an industry standard formula for comparative testing of polymer systems. Improvements across all crude Hevea NRL samples, the purified NRL feedstock served as the baseline. See also FIG. 10, 11 & 12 and Table 1, 2 & 3.

[213] Compounded Strength: Pot Life. This tests the shelf life of the compounded NR before it is used in manufacturing of the rubber product. Pot Life across the purified NRL lots averaged 4.65 weeks as compared to an average of 2.98 weeks for non-purified NRL lots/samples, which decreased at about 12% and then rapidly decreased to 31.6% by mid-week three.

[214] Uncompounded Mechanical Stability Test (MST). This tests the stability of the latex prior to compounding. Steady state for MST testing compared to crude Hevea NRL samples held for a five (5) week period.

[215] Coagulum Percentage (%BW). This test for reduced or comparative levels of coagulum. As per the testing of samples as delivered from the supplier and an appropriate period of eight (8) weeks after production of the purified NRL test materials. A decreased amount of coagulum may reference the addition of surfactant in the stability lot. A maturation period after production was truncated. While for the samples received it is unknown as to the maturation period after centrifugation at the plantation. See also Table 1, 2 & 3.

[216] Physical Properties of Purified NRL after Impurities are Reincorporated. The effect impurities removed during the purification process have on when reincorporated (added back in) to purified NRL. A portion of the impurities accumulated from the disc stack, bowl and heavy phase discharge were retained and reincorporated back into a sample of purified NRL production at various levels of the Step 1-4 process as described herein. Both compound and uncompounded materials were tested to evaluate the effect of impurity loading on physical performance properties of dipped articles. Specific results of these tests follow. See also FIG.1.

[217] Tensile, Compounded. In general, the baseline article produced used the standard compound formula and chemicals (except green testing) with maturated to purify NRL. Other samples taken from the same purification process lot were compounded with differing percentages of impurities with four articles produced and averages noted. As impurities were reincorporated to the purified NRL, the physical properties declined significantly, signifying a correlation between purity levels and performance levels. The test was designed to accept a range of reincorporated impurities: 1.5%, 1.75% and 2.5%. Moreover, for each sample of purified NRL used, four samples were produced and tested with the average noted. See also FIG.11, Tables 1, 2 & 3.

[218] Elongation, Compounded. Test results as described above. See also FIG.14 and Tables 1, 2 & 3.

[219] Green Strength Tensile as Uncompounded. The purified NRL sample with incorporated impurities performed similar to crude Hevea NRL from prior testing. Additionally, a comparison to the baseline (0 impurities) was performed for the reincorporated purified NRL sample at two different reincorporated percentages: 1.5% and 2.5%. Physical green performance was found similar to that of the crude Hevea NRL with the higher loading significantly worse. A cast sample was produced by pouring the impurity rich NRL into a mold with 1.5mm thickness. The sample was oven dried at 60C for one hour followed by a few more hours at ambient of 20C. The article was removed from the mold and flipped to ambient temperatures until fully dried. It is noteworthy, that some crude Hevea NRL lots (4 in total) contained percentages of Non-rubber Content (NRC) above that of the industry standard and what is found to be typical, or about 2%. Six of the ten lots tested showed green strength as described on the lot individual certificates of analysis (CoA) at an average of 2.23%NRC. Of the ten lots tested, four showed elevated NRC with an average of

3.87% to a high of 4.26%NRC, which is above the 2% industry standard and not the same value noted on the lot CoA. See Table 1, 2 & 3.

[220] Improved/Increased Centrifuge Operating Period by Means of a CIP System.

This test was performed to determine whether there was an operation efficiency changes with increased purification centrifuge operation times. It was noted that as Mean Time Between Servicing due to loaded bowl and reduced output for light phase discharge. In addition, wasted 'cream' in the bowl cover light phase discharge is reduced due to capture by the CIP. See also FIG. 18 and 19.

Results

[221] Natural rubber latexes were used for testing as described in the Tests section above and described in the Results section herein. Certain NRL samples were taken prior to processing the latex as in purification described herein as well as during the purification process and after. The tests below unless indicated test properties of compounded natural rubber. All samples were compounded using a typical dipped article, which was then used for physical testing. Protein content was performed on uncompounded rubber or rubber latex since methods for measuring protein of a compounded article is not reliable and not indicative of the protein levels actually in the natural rubber. Both compounded and uncompounded latexes were evaluated in a similar manner. Table 1 & 2 are a summary of certain of the tests and samples described herein. Figures 4 and 9-19 also are results of certain of these tests described herein.

[222] The compound formula used to test the samples consists of 100 NRL emulsion (purified, crude, or low protein), 0.1 Calsoft L-40, 5 Bostex 827, and 1.0 Wingstay L. This compound is a basic compound that utilizes a master batch cure package available from Akron Dispersions (Bostex 827), which is a typical NR cure package for Hevea. This provides acceptable and comparable properties. Twelve dipped sample articles were produced from each compounded batch and tested in the laboratory for tensile, elongation and modulus properties. The data in Table 1 below is an average across all twelve samples produced and tested including those samples with incorporated impurities. The baseline purified NRL was compounded and then separated into four, 1 L samples where different percentages of the impurities were added back in as described above under the testing (1.5%, 1.75%, 2.75%)

Table 1: Properties of Purified Elastomeric Natural Solid or Latex Rubber Compared to other Crude Natural Rubber Source Materials

	Purified NRL (YPP) LA	Typical Hevea HA	Typical Hevea LA	Typical Double Centrifuge	Low Protein Brand V Typical
Material Type	Emulsion	Emulsion	Emulsion	Emulsion	Emulsion
Stabilizer	Ammonia	Ammonia	LATZ	Ammonia	Ammonia
Total Solids Content (TSC), wt. %	63.71	61.00 – 63.00	61.00 – 63.00	60.5	61.09
Dry Rubber Content (DRC), wt. %	63.67	59.00 - 61.00	59.00 - 61.00	60	60.15
Non-Rubber Content (%)	0.04%	up to 2.0%	up to 2.0%	up to 0.5%	1%
Alkalinity - as NH₃	0.4	0.7	0.7	0.60 - 0.78	0.7
Viscosity @ 60% TSC, cps.	95	50 – 100	50 – 100		
Sludge, wt. %	Non-detect	<0.100	<0.100	Not Specified	<0.100
Coagulum, wt. %	≤0.002%	<0.0080	<0.0080	0.01	0.006
pH	11	10.0 – 11.0	10.0 – 11.0	10.85	10.65
Mechanical stability @ 55% TSC, sec.	730*	800 – 1500	800 – 1500	800 - 1200	1230
Odor - dried film	1				
Odor, Emulsion	Slight Ammonia	Strong Ammonia	Ammonia	Strong Ammonia	Strong Ammonia
Color - latex	Bright white	off white	off white	white	off white
Color - Air Dried Film	Clear	Translucent yellow	Translucent yellow	Translucent yellow	Translucent amber
Elongation at Break, %, Min	844	789			778
Preservation	Ammonia	Ammonia, zinc oxide	Ammonia, Zinc Oxide, TMTD	Ammonia, zinc oxide	Ammonia, zinc oxide
Total Protein	<50ug/g	8,685ug/g	6,988ug/g	6,109ug/g	1,965ug/g

A dipped article was produced from each on day one, then after three days of pot maturation, and then a series of four test articles were produced from each test sample, cured, dried and tested for their respective physical properties, the results of which are described in more detail below. Additionally, uncompounded cast films were produced to test green strength.

5

Table 2: Protein Content of Purified NR Compared to Un-purified NR

	Purified NR	Crude Hevea	Low Protein
	Protein Content		
Total Protein Wet Emulsion	50/ug/g emu	6,992/ug/g emu	1,965/ug/g emu
Antigenic	3	388	165
Post Compound Rise³	67/63	10,266 / 11,887	2,272 / 2,309
Total Protein Film	<10	NA	NA

[223] Table 2 describes average, high and low protein content over three samples per material type (n=3). Post compound rise is an indication of the stability of the material's protein content to increase as a result of surfactant leaching of protein solubilization. Test is performed two (2) and four (4) weeks after the surfactant is added.

[224]

15 **Table 3: Tensile Strength of Purified NR Compared to Unpurified or Low Protein NR**

	Purified NR	Crude Hevea	Low Protein	Purified Low Protein
Formula	Tensile Strength (MPa)			
S1	35.1	32.2	26.4	28.9
S2	36.8	31.4	24.5	29.7
S3	36.4	30.8	22	25.2
S3-X1	39.7			

[225] S3-X1, X2 are purified NR produced from methods substantially as described herein, but are compound formulas to enhance end-product performance properties in certain areas and do not necessarily demonstrate total optimization of the methods disclosed herein.

Table 4: Green Strength & Color of Purified NR Compared to Unpurified NR

	Purified NR	Crude Hevea	Low Protein	Purified Low Protein
Tensile MpA	8.2	5.1	1.5	2.4
Color	Clear	Yellowish	Deep Yellowish	Deep Yellowish

Table 5: Elongation of Purified NR Compared to Unpurified NR

	Purified NR	Crude Hevea	Low Protein	Purified Low Protein
	Elongation %			
Set 1	1,400	1,155	1,105	1,186
Set 2	1,423	1,198	1,001	1,298
Set 3	1,445	1,009	930	1,000
Set 3-X1	1,509			

5

[226] S3-X1, X2 are purified NR produced from methods substantially as described herein, but are compound formulas to enhance end-product performance properties in certain areas and do not necessarily demonstrate total optimization of the methods disclosed herein.

Table 6: Modulus of Purified NR Compared to Unpurified NR

	Purified NR	Crude Hevea	Low Protein	Purified Low Protein
	Modulus			
Set 1	2.07	3.89	4.52	4.01
Set 2	1.9	4.03	4.55	3.98
Set 3-X1	1.33	NA	NA	NA

15

[227] The lower the Modulus (Mpa) the softer the material. For example, the Purified NR of the present invention in Table 6 is softer than the Crude Hevea, Low Protein or Purified Low Protein natural rubber commercial samples. Low modulus correlates with high elongation; and low modulus and high elongation correlates with lower tensile strength. Hence, the methods disclosed herein disclosing methods for production of a purified NR with high tensile strength (Table 3) and low modulus (Table 6) is markedly different and surprising over existing commercial unpurified and purified NR brands. The purified NR

disclosed herein is therefore softer and preferred while at the same time has high mechanical strength and stability. Until this disclosure herein, such a purified NR with these physical properties has not been described.

[228] Table 7 describes the tensile, elongation and modulus of the purified NR

5 disclosed herein compared to unpurified NR.

Table 7: Average Tensile, Elongation & Modulus of Crude (Unpurified) and Purified NRL

	Crude / Unpurified NRL	Purified NRL
Cure Time:	20-25 min	20-25 min
Cure Temp:	105°C	105°C
Tensile	~27.5 Mpa	~33 Mpa
Elongation	~680%	~870%
Mod @ 200%	~2.0	~1.1
Mod @ 500%	4.4	3.7

[229] The invention of this application has been described above both generically
 10 and with regard to specific embodiments. It will be apparent to those skilled in the art that various modifications and variations can be made in the embodiments without departing from the scope of the disclosure. Thus, it is intended that the embodiments cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

15

WHAT IS CLAIMED IS:

1. A purified deproteinized natural rubber emulsion comprising less than about 50 ug/g of total protein.

2. The purified deproteinized natural rubber of claim 1, wherein the purified deproteinized natural rubber tensile strength is at least 15% greater as compared to unpurified or low-protein natural rubber about.

3. The purified deproteinized natural rubber of claim 1, wherein the purified deproteinized natural rubber green strength is about 60% greater as compared to unpurified or low-protein natural rubber.

4. The purified deproteinized natural rubber of claim 1, wherein the purified deproteinized natural rubber softness (Modulus) is about 45% less than unpurified or low-protein natural rubber.

5. The purified deproteinized natural rubber of claim 1, wherein the purified deproteinized natural rubber has increased tensile strength and softness as compared to undeproteinized or low-protein natural rubber.

6. A method for producing purified natural rubber substantially free of proteins, the method comprising:

a. purifying field or centrifuge rubber tree latex in a high speed centrifuge comprising at least a dilution liquid with the latex mixture in a ratio of 1:1 to 1:17, wherein the liquid dilution comprises an anionic high solubilizing surfactant and an alkaline inorganic compound, wherein the mixture extracts non-rubber particles comprising proteins from the rubber particles in the latex; and

b. purifying the mixture using at least one centrifuge by separating and collecting the rubber particles, wherein the rubber particles are about 99% free of proteins,

thereby producing a purified natural rubber substantially free of proteins.

7. A method for producing the purified deproteinized natural rubber of claim 1-5, comprising the steps of:

a) obtaining a batch of rubber tree or low-protein latex;

b) washing the latex in a ratio 1:1 to 1:17 comprising an anionic solubilizing surfactant and an alkaline inorganic compound;

c) centrifuging the composition of step (b), wherein centrifuging the rubber separates the rubber particles from the non-rubber particles; and

d) collecting the purified deproteinized natural rubber. The method of claim 6-7, wherein the alkaline inorganic compound is potassium hydroxide (KOH).

8. The method of claim 6 or claim 7, wherein the anionic solubilizing surfactant is a disulfonate.

5 9. The method of claim 8, wherein the disulfonate is a Sodium Hexadecyl Diphenyl Oxide Disulfonate.

10. The method of any of claims 6 to 9, wherein the non-rubber particles includes proteins, oils, fats, metals, dirt and other non-rubber particles.

10 11. The method of claim 10, wherein the proteins comprise Type 1 latex allergen proteins.

12. The method of any of claims 6 to 11, wherein the dilution liquid and latex mixture is in on or more containers proximal to the centrifuge.

15 13. The method of any of claims 6 to 12, wherein the centrifuge is interconnected to the one or more tanks and comprise of one or more control valves or locks and one or more pumps that control the flow of solution to the centrifuge.

14. A scalable method for producing purified natural rubber substantially free of protein, the method comprising:

20 connecting a centrifuge to at least one solution container comprising natural rubber latex and a washing solution, wherein the centrifuge and the containers are interconnected by one or more control valves or pumps to control the flow rate of the solution container to the centrifuge;

opening at least one control valve to flow the solution to the centrifuge, wherein the flow is at a rate of about 1 to 10 gallons per minute (gpm);

25 centrifuging the solution to separate the rubber and non-rubber particles comprising the proteins and collecting the rubber particles; and

cleaning the centrifuge while continuously and simultaneously separating the rubber and non-rubber particles,

thereby scaling production run time for producing purified natural rubber.

30 15. The method of claim 14, wherein the method is modular and about 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or more centrifuges are interconnected to one or more solution containers.

16. The method of claim 14 or claim 15, wherein the method further comprises one or more pumps interconnected to the centrifuge or one or more containers.

17. The method of any of claims 14 to 16, wherein the centrifuge is cleaned and the wash expelled and collected, thereby extending the operation run times.

18. A deproteinized natural rubber emulsion substantially about 99% free of soluble rubber proteins.

5 19. The deproteinized natural rubber of any of claims 1 to 5, or claim 18, wherein the rubber is a solid or a latex emulsion.

20. The deproteinized natural rubber of any of claims 1 to 5, or claim 18 or claim 19, wherein the concentration of protein is between about 10 ug/g to about 1900 ug/g, or is less than about 1900 ug/g.

10 21. The deproteinized natural rubber of claim 20, wherein the concentration of protein is between about 10 ug/g to about 100 ug/g, or is less than about 100 ug/g.

22. The deproteinized natural rubber of claim 21, wherein the concentration of protein is about 50 ug/g.

15 23. The deproteinized natural rubber of any of claims 1 to 5, or any of claims 18 to 22, wherein the tensile strength and modulus are increased as compared to proteinized or low proteinized rubber.

24. The deproteinized natural rubber of claim 23, wherein the rubber tensile strength is between about 30 MPa to about 40 MPa, or is greater than about 30 MPa.

20 25. The deproteinized natural rubber of any of claims 1 to 5, or any of claims 18 to 24, wherein the rubber maintains a pot life greater than 2 weeks.

26. The deproteinized natural rubber of claim 25, wherein the rubber maintains a pot life greater than 3 weeks.

27. The deproteinized natural rubber of any of claims 1 to 5, or any of claims 18 to 26, wherein the rubber maintains an alkaline pH stability for 3 weeks or more.

25 28. The deproteinized natural rubber of claim 27, wherein the rubber maintains an alkaline pH stability for 5 weeks or more.

29. The deproteinized natural rubber of any of claims 1 to 5, or any of claims 18 to 28, wherein the total solid content (TSC) in the rubber is between about 50% to about 65%, or the total solid content (TSC) in the rubber is greater or more than about 50%.

30 30. The deproteinized natural rubber of claim 19, wherein the rubber has greater green strength as compared to proteinized rubber.

31. The deproteinized natural rubber of any of claims 1 to 5, or any of claims 18 to 30, wherein the rubber is substantially odorless and colorless.

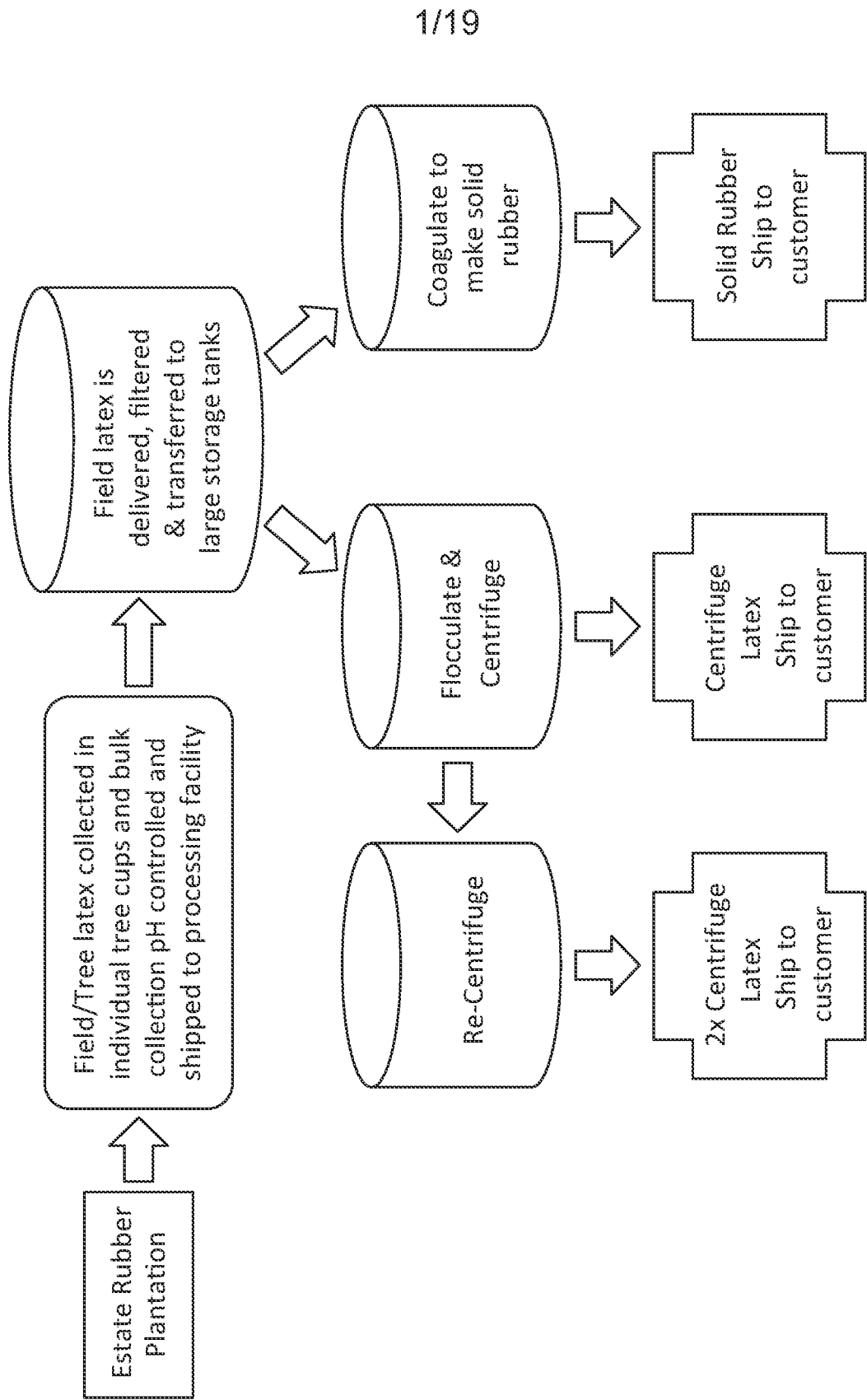


FIG. 1

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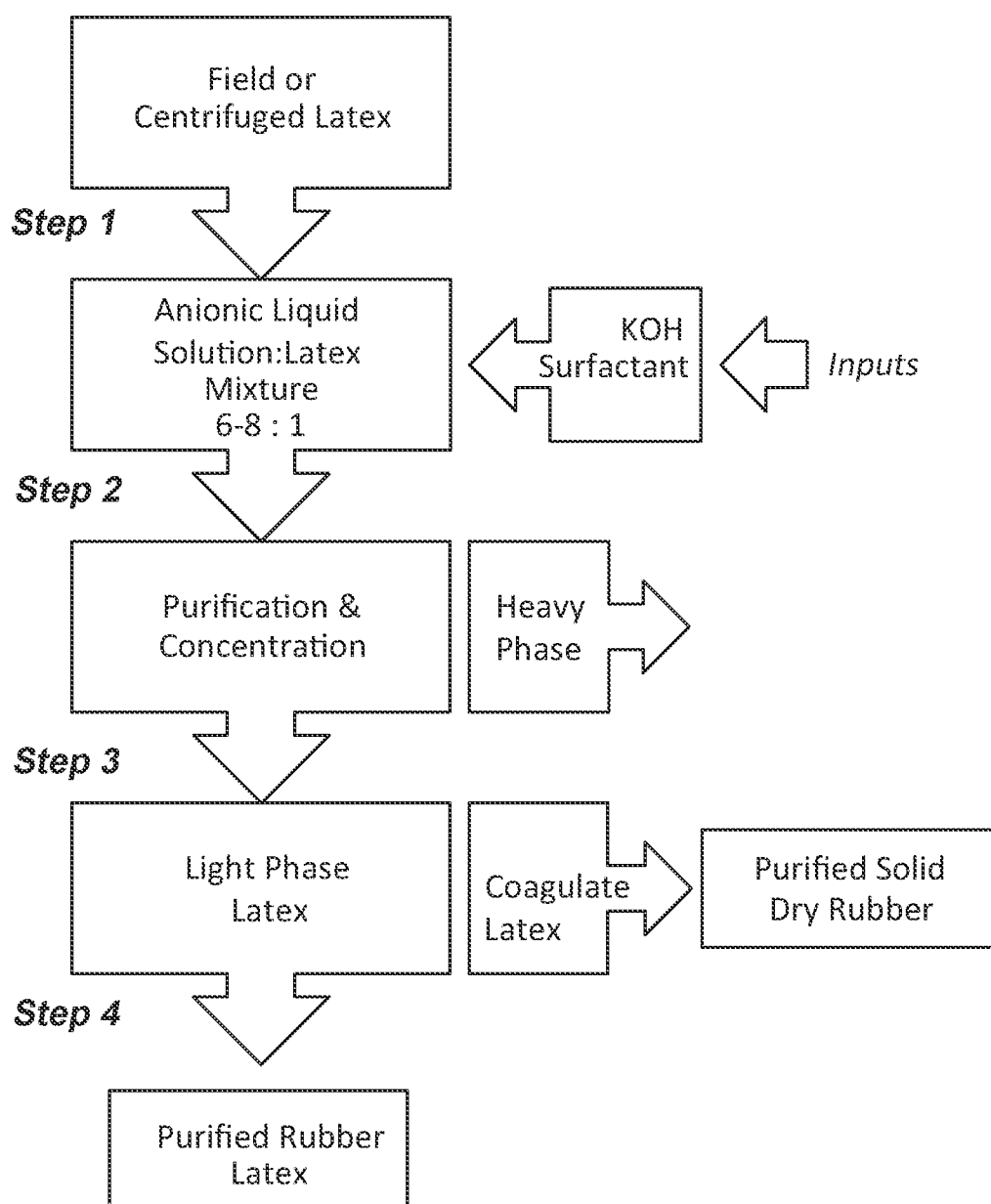


FIG. 2

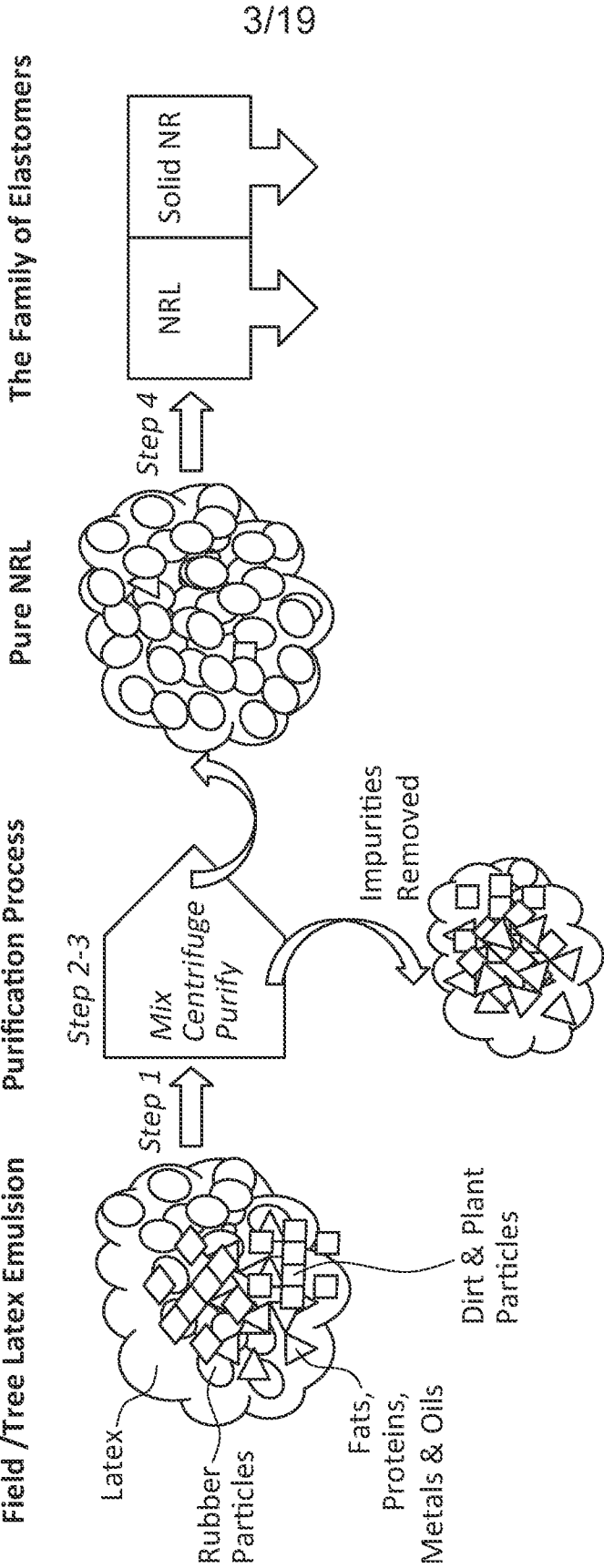


FIG. 3

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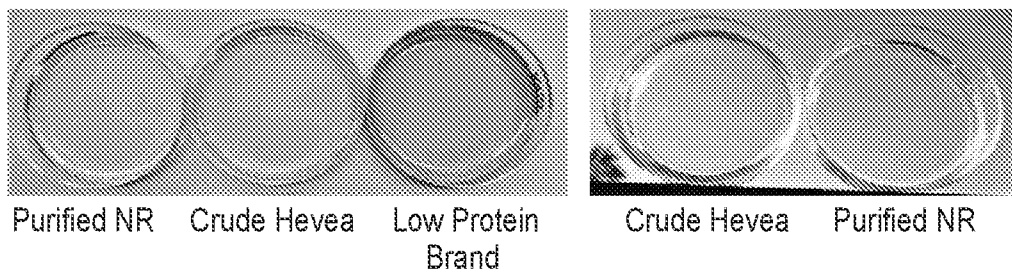


FIG. 4A

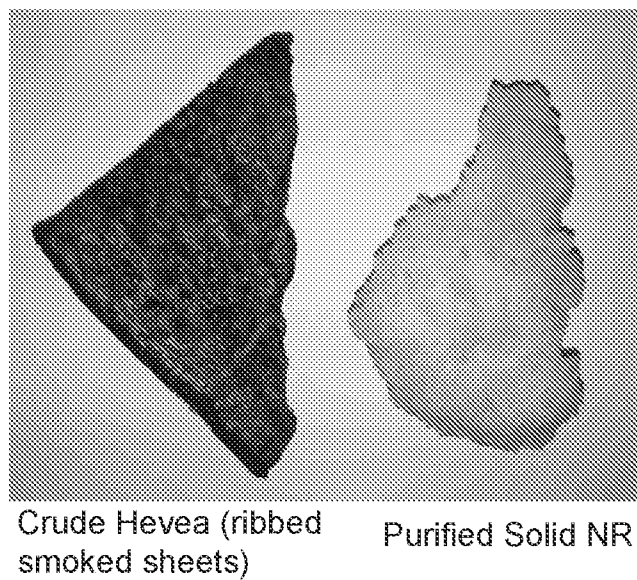


FIG. 4B

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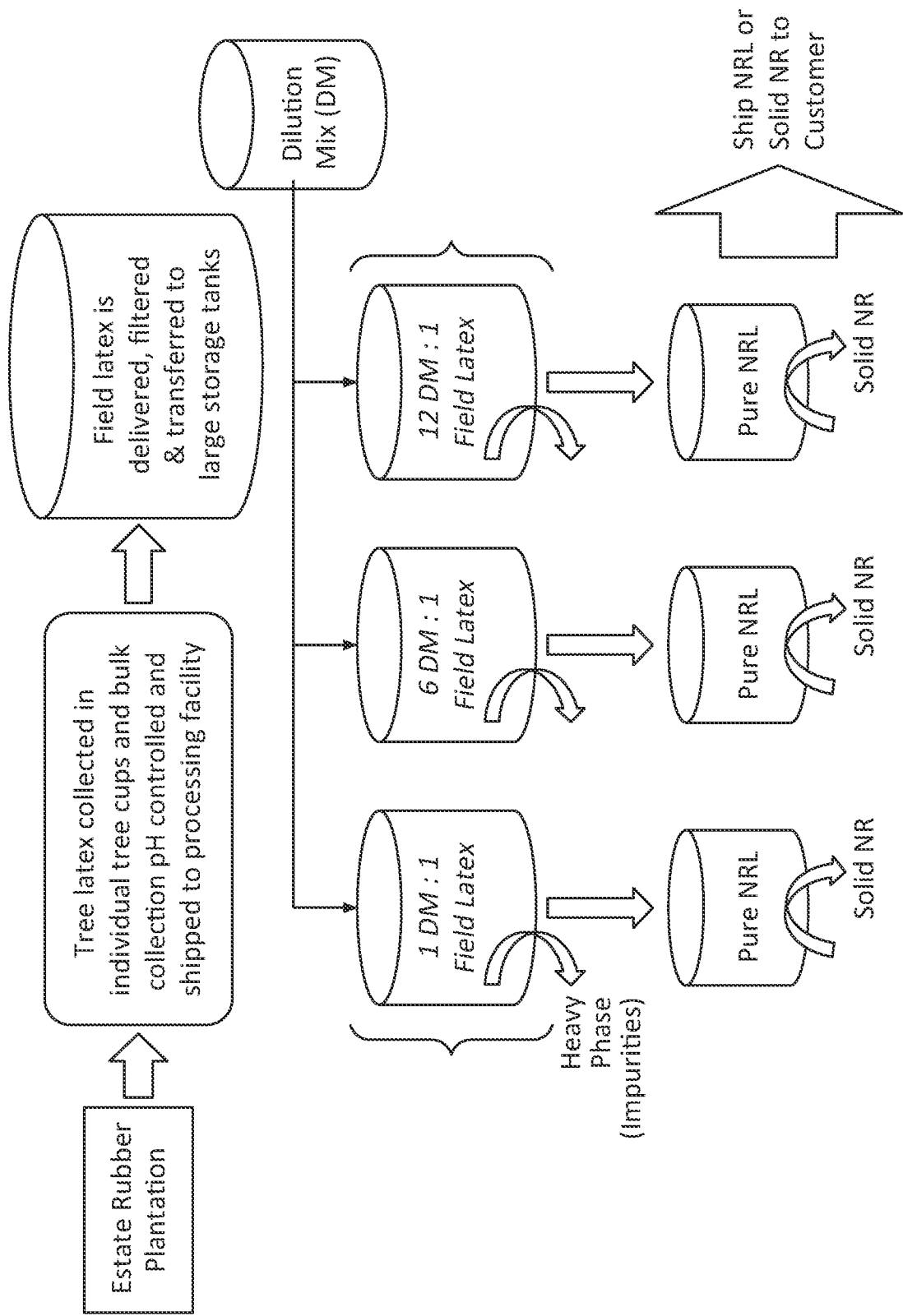


FIG. 5

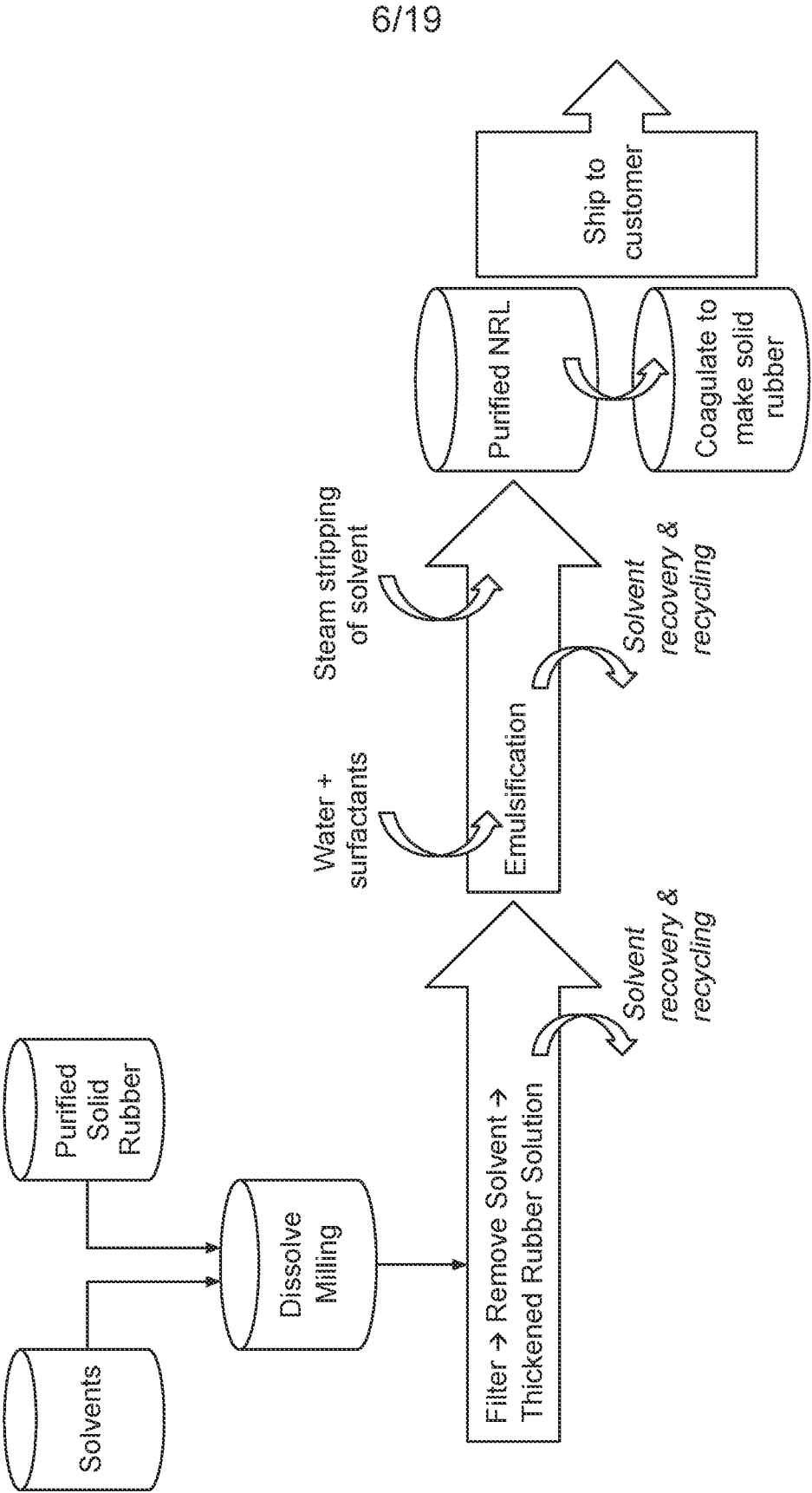


FIG. 6

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CIP System

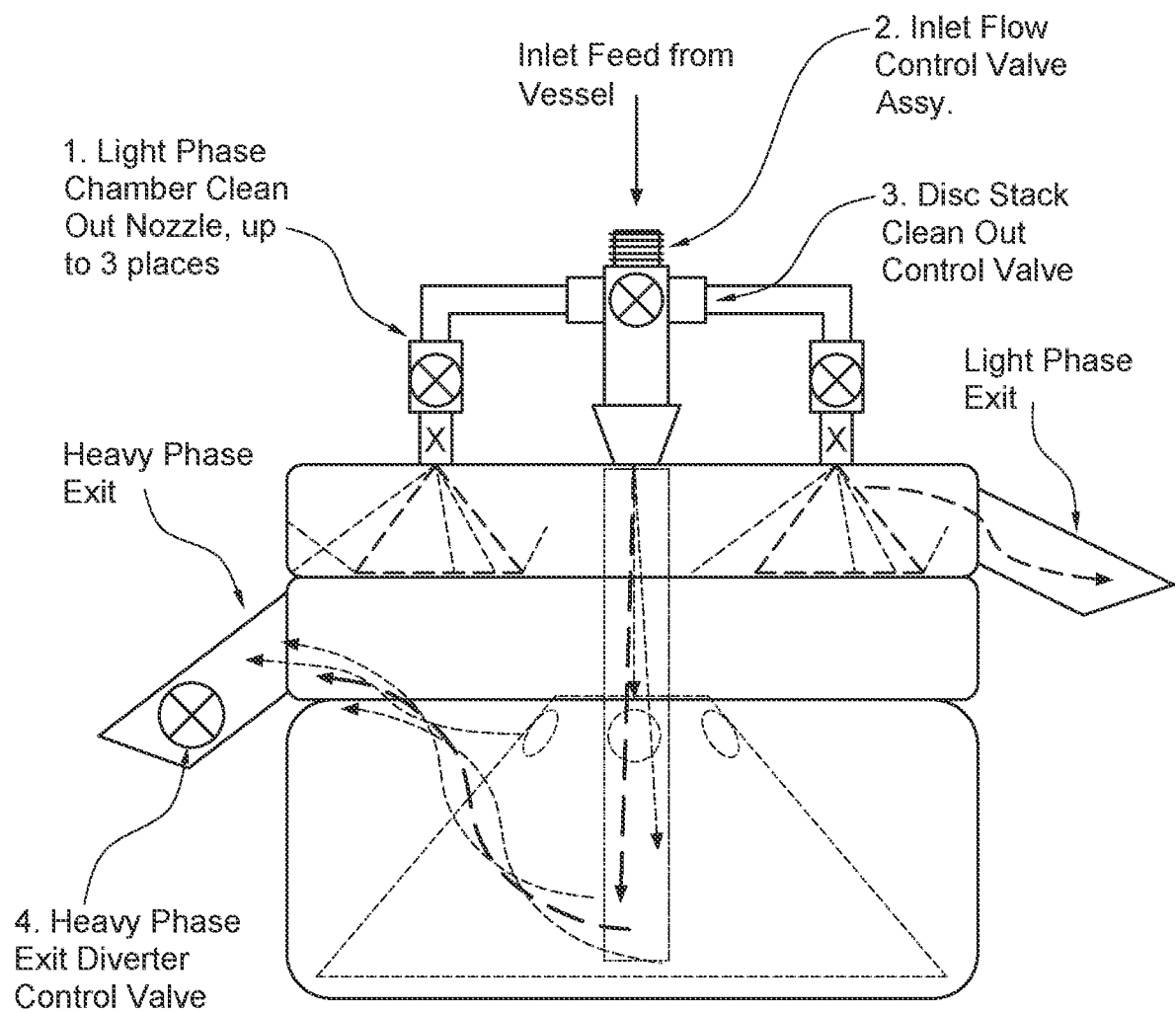


FIG. 7

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Centrifuge CIP System Schematic

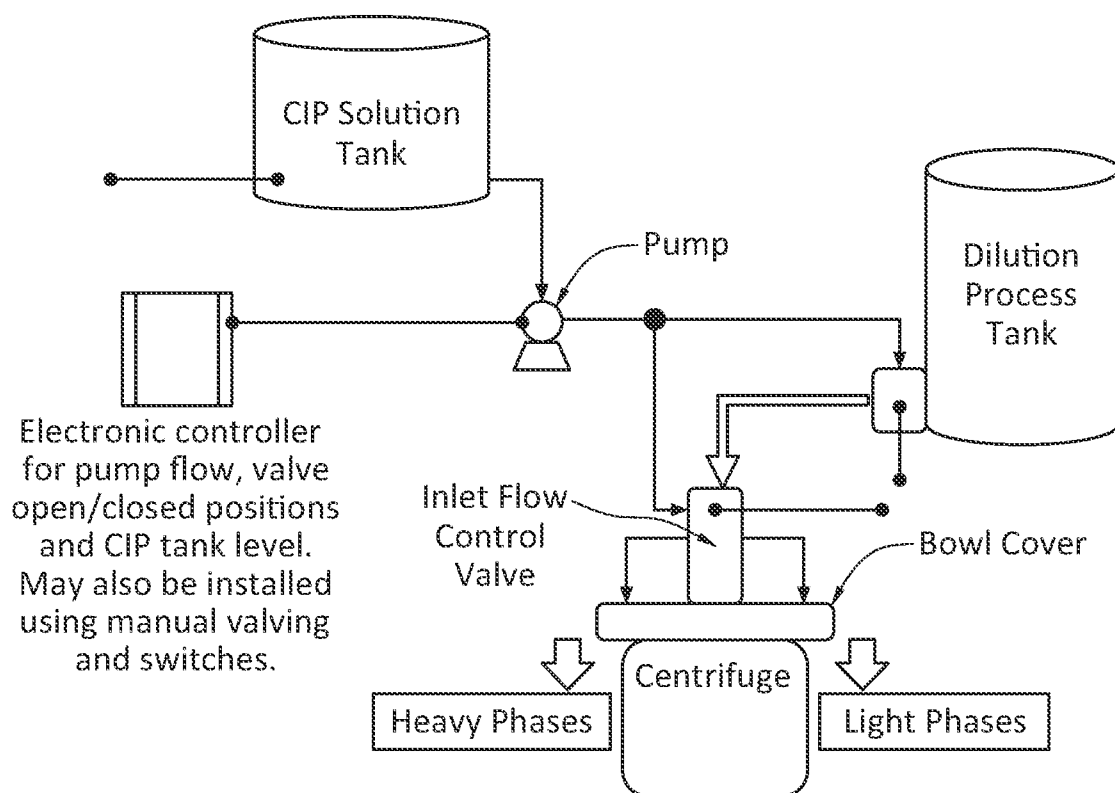


FIG. 8

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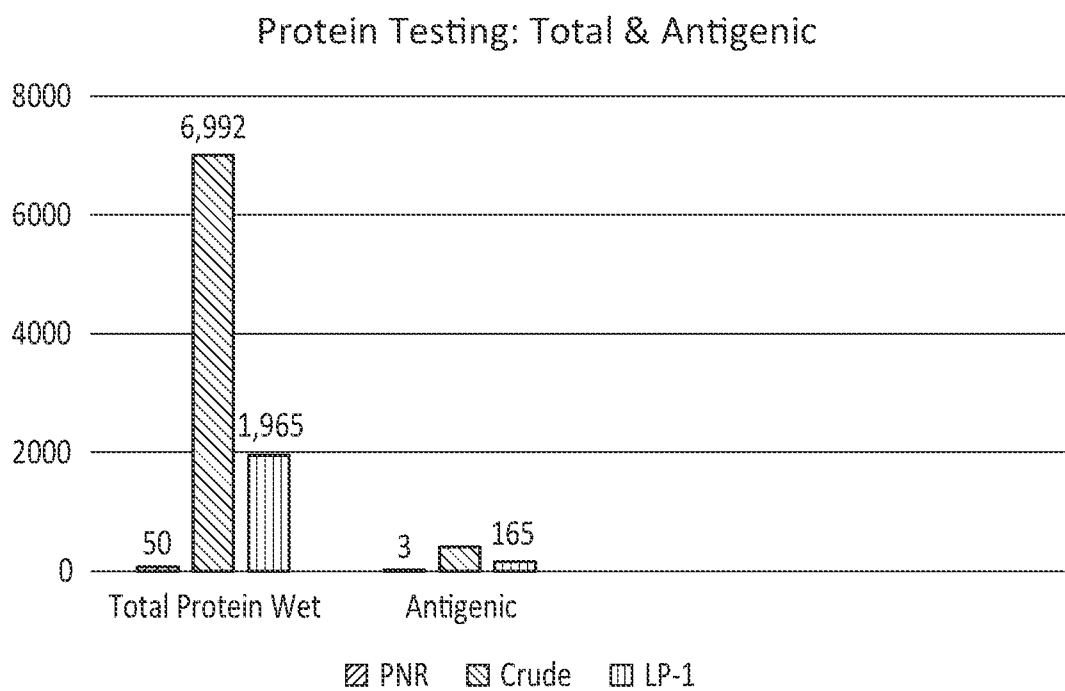


FIG. 9

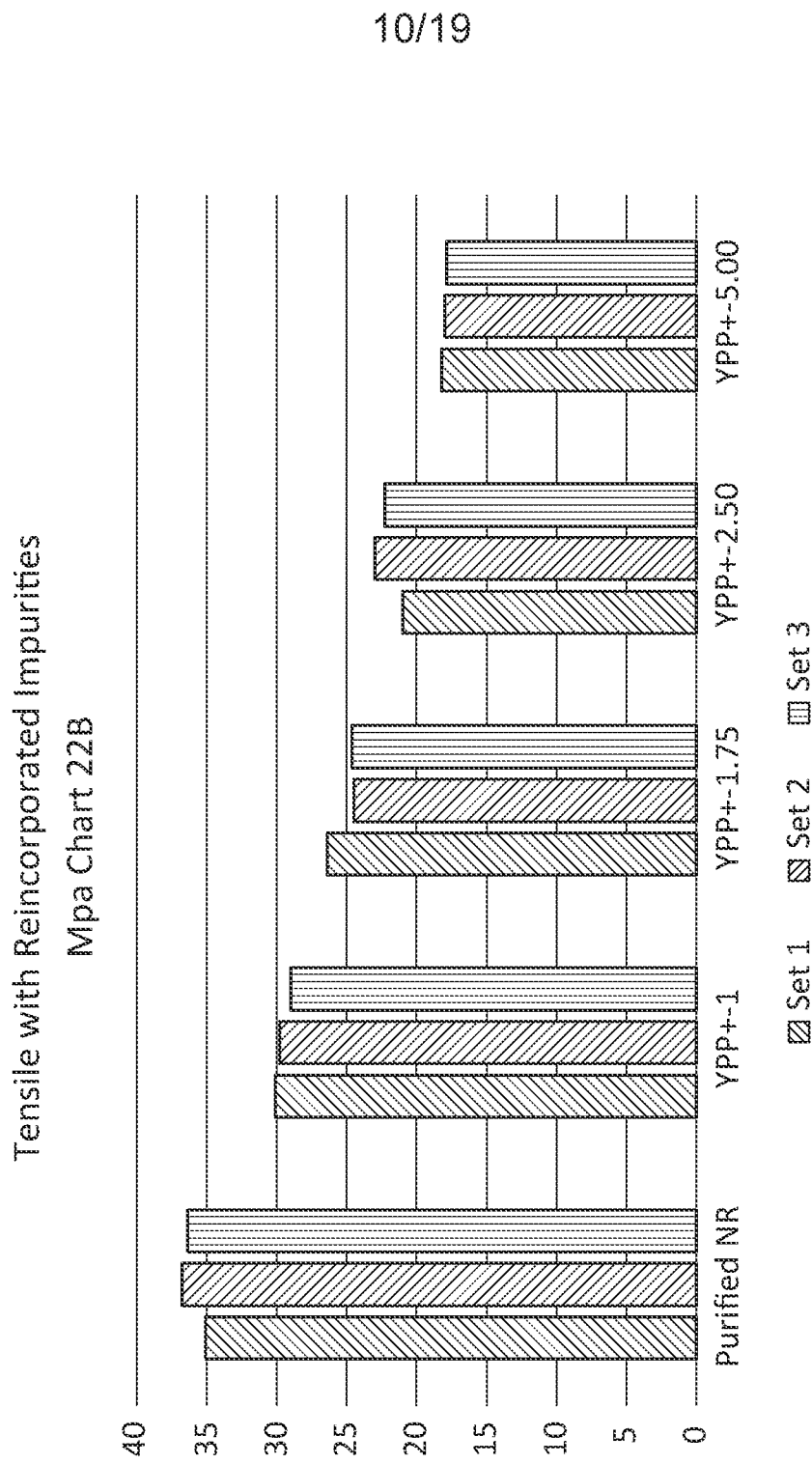


FIG. 10

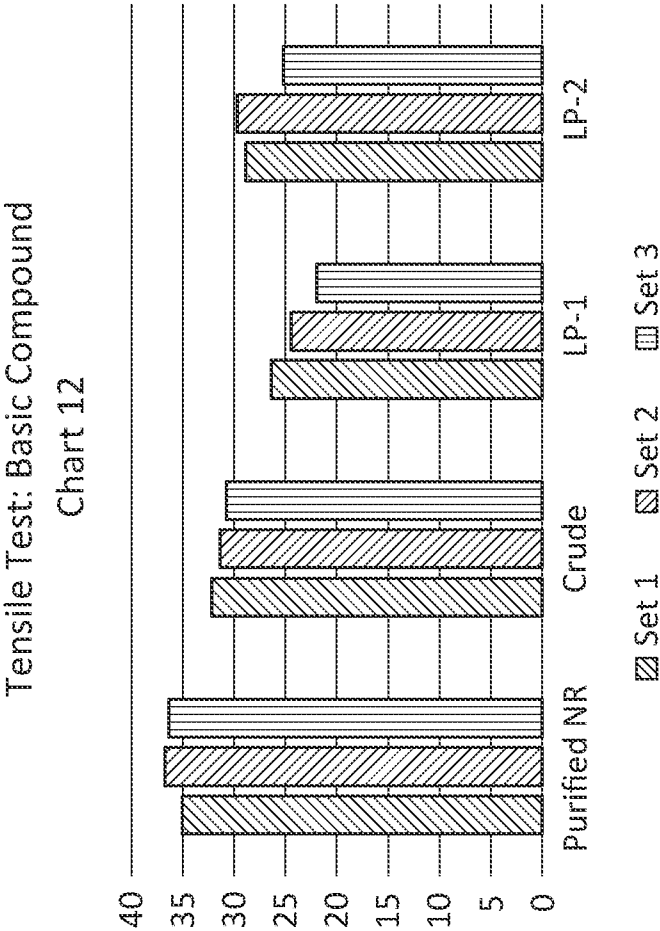


FIG. 11

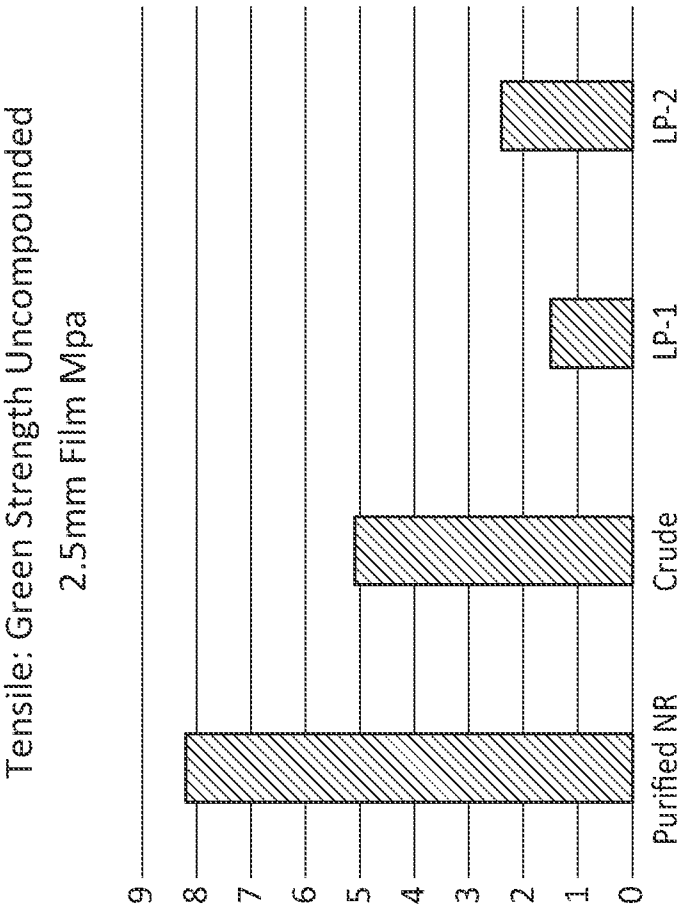


FIG. 12

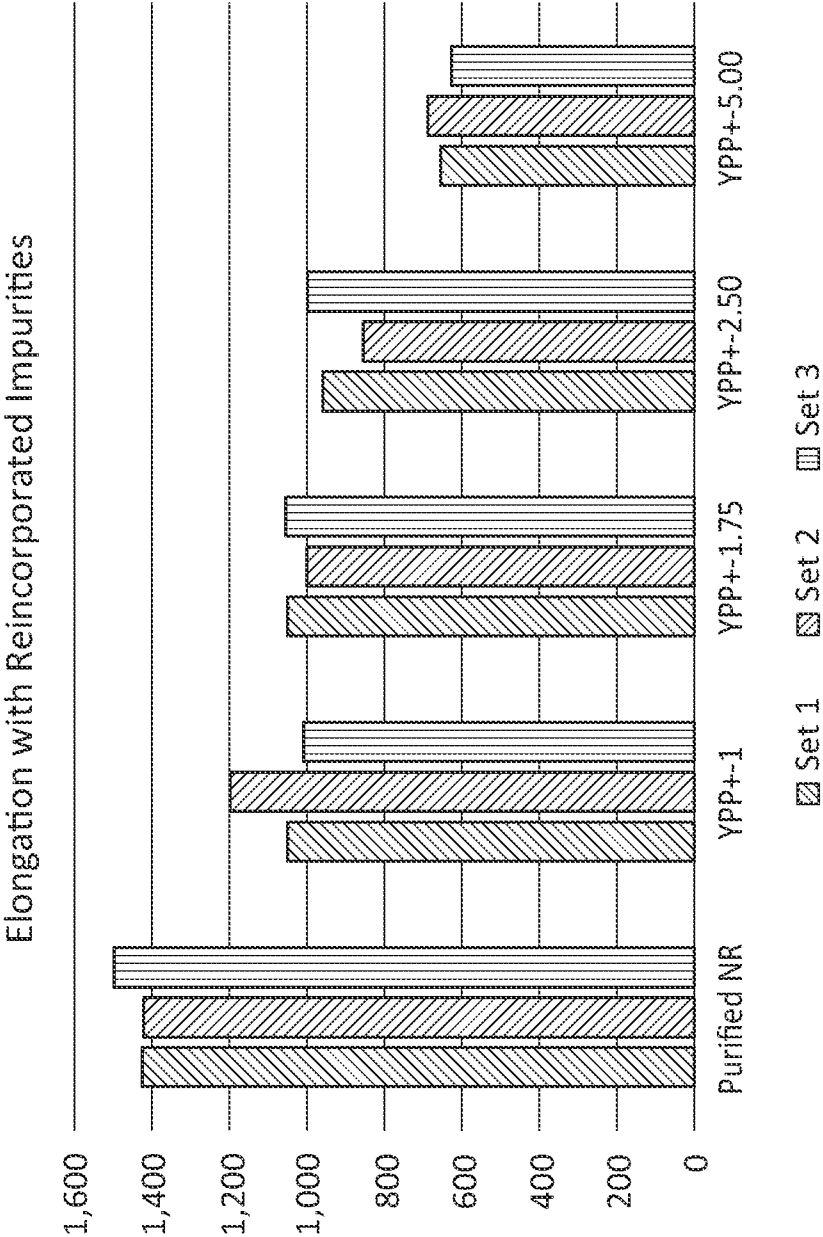


FIG. 13

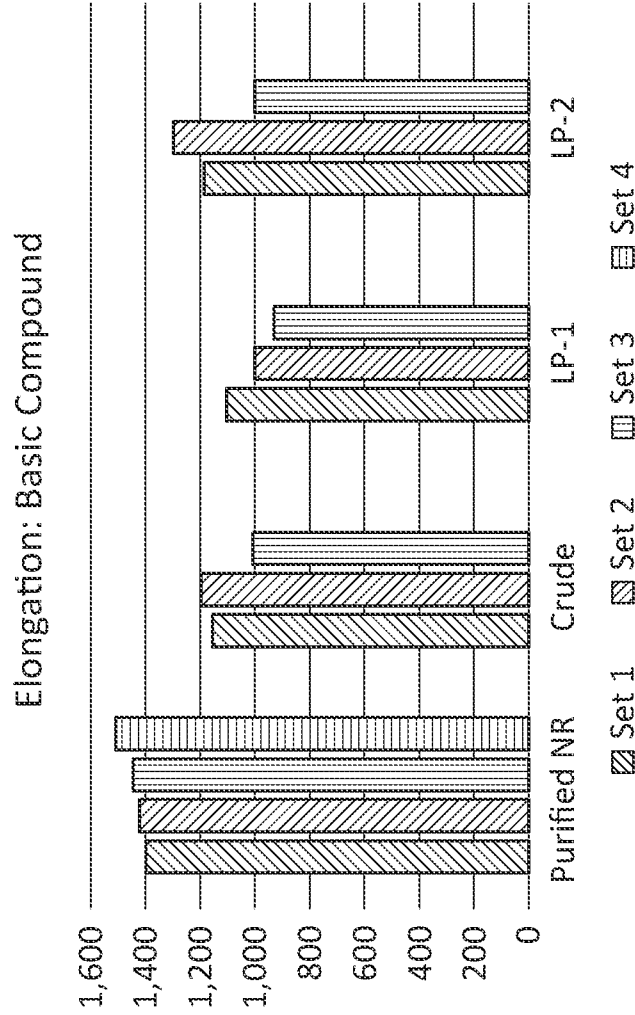


FIG. 14

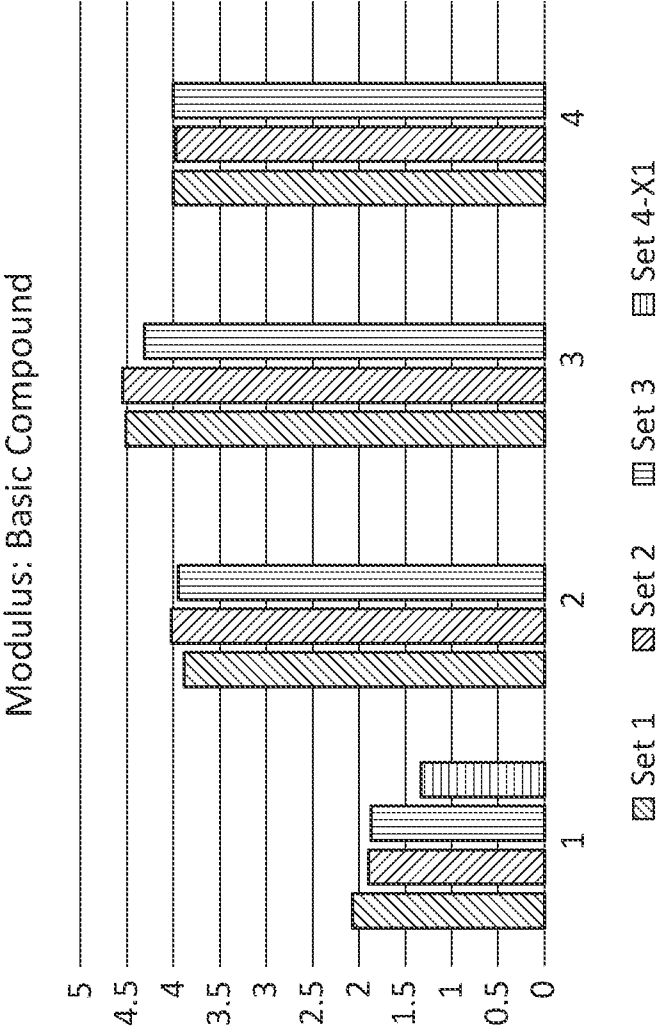


FIG. 15

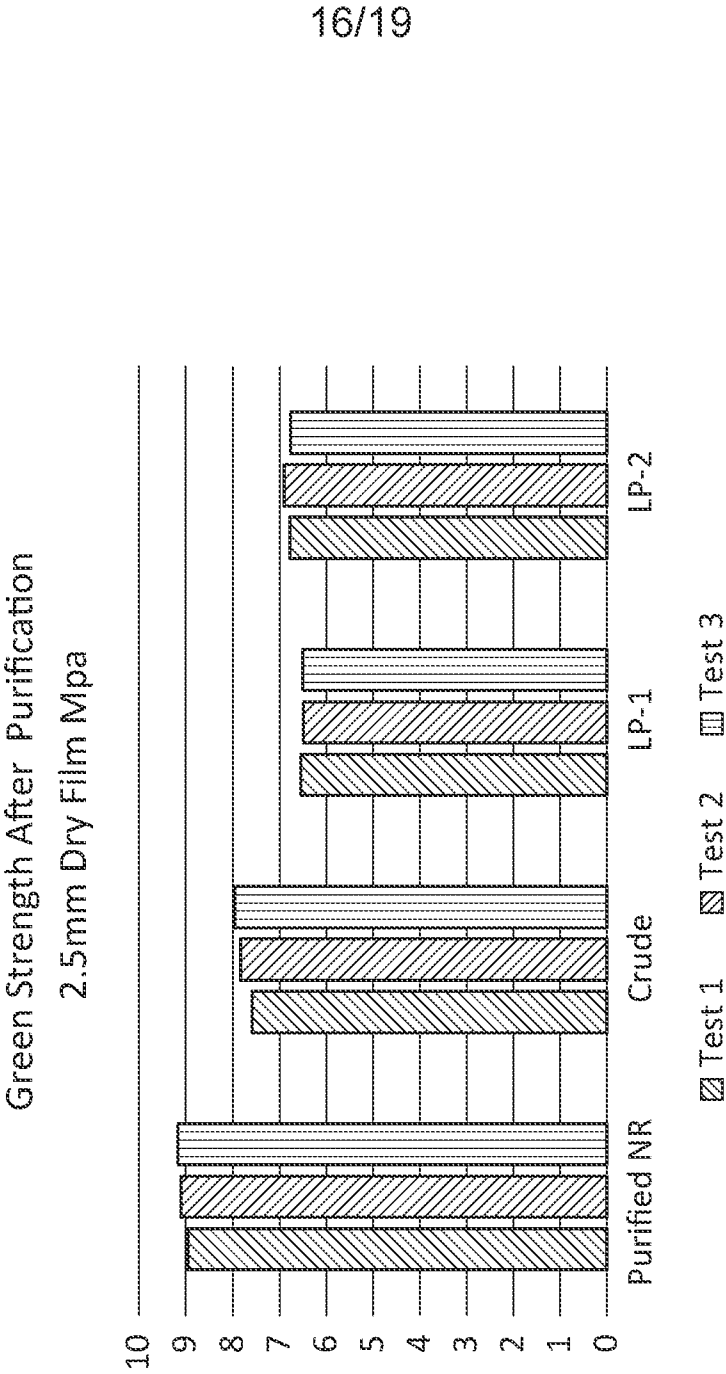


FIG. 16

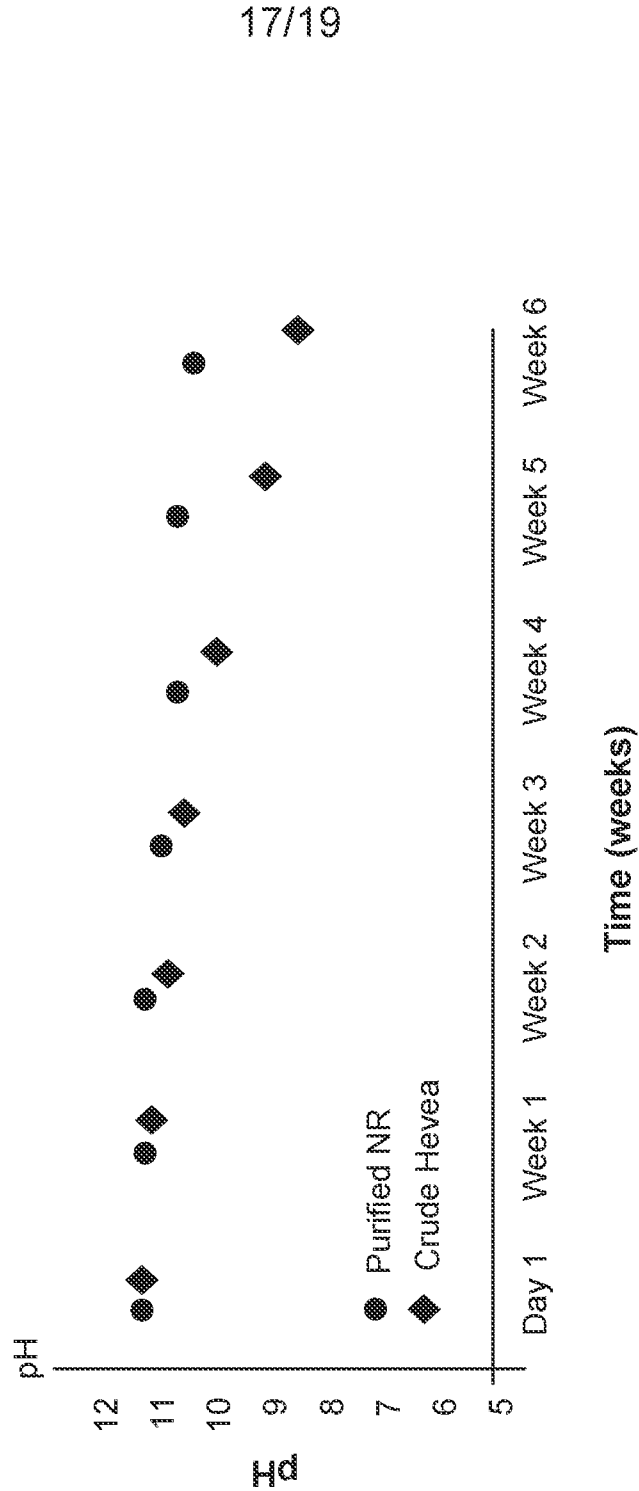


FIG. 17

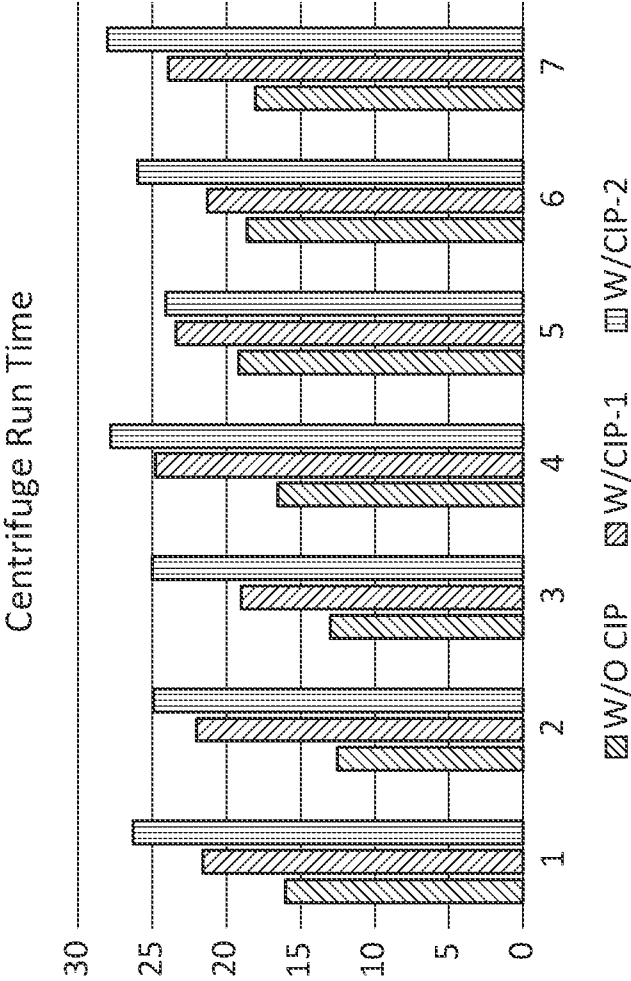


FIG. 18

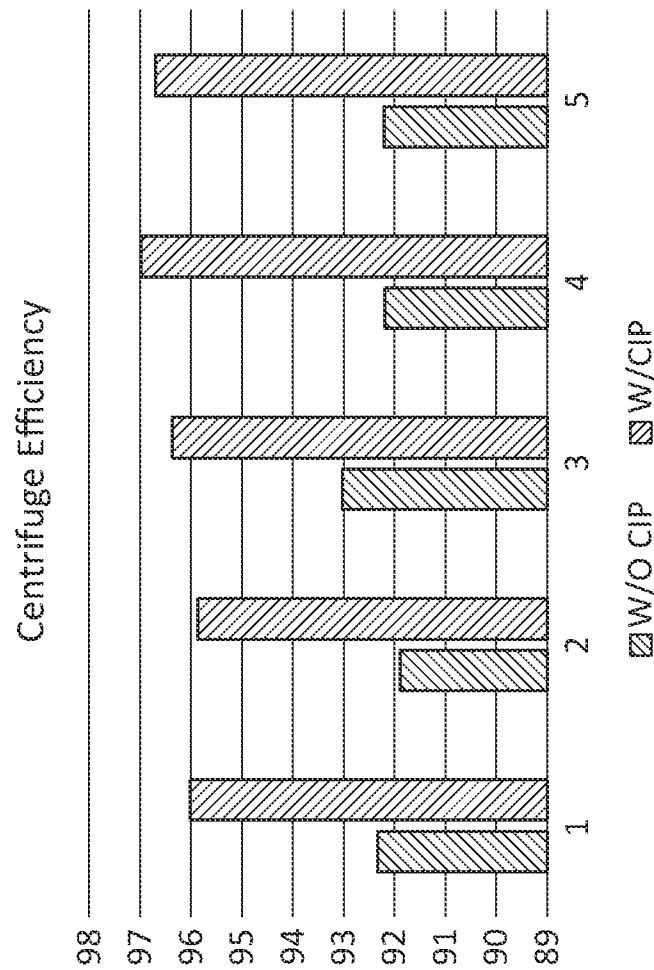


FIG. 19

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2021/040085

A. CLASSIFICATION OF SUBJECT MATTER C08C 1/02(2006.01)i; C08C 2/02(2006.01)i; C08L 7/02(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08C 1/02(2006.01); B04B 5/12(2006.01); C08C 1/04(2006.01); C08J 9/00(2006.01); C08L 7/00(2006.01); C08L 9/06(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: deproteinized, purified, centrifugation, natural rubber, latex, strength		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007-126562 A (HIGASHI KAGAKU KK) 24 May 2007 (2007-05-24) abstract; paragraphs [0001]-[0025]	1-7,18-19,30
Y		14-16
Y	EP 0758925 B1 (BAPTISTA, F. A. et al.) 04 November 1998 (1998-11-04) claims 6-7	14-16
A	JP 2001-081107 A (SUMITOMO RUBBER INDUSTRIES, LTD. et al.) 27 March 2001 (2001-03-27) the whole document	1-7,14-16,18-19,30
A	JP 2000-007708 A (YUKIGAYA KAGAKU KOGYO KK) 11 January 2000 (2000-01-11) the whole document	1-7,14-16,18-19,30
A	US 2016-0075863 A1 (SUMITOMO RUBBER INDUSTRIES, LTD.) 17 March 2016 (2016-03-17) the whole document	1-7,14-16,18-19,30
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 October 2021		Date of mailing of the international search report 26 October 2021
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer KWON, Yong Kyong Telephone No. +82-42-481-3371

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

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

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

2. ☒ Claims Nos.: **9, 11, 21-22, 24, 26, 28**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims 9, 11, 21-22, 24, 26, 28 are unclear, because they refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: **8, 10, 12-13, 17, 20, 23, 25, 27, 29, 31**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2021/040085

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
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				MY	139517	A	30 October 2009
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				JP	5650794	B2	07 January 2015
				US	9862814	B2	09 January 2018
				WO	2014-188901	A1	27 November 2014