A glove, including a polymeric, elastomeric, or latex composition, having a water-based emulsion of a polyisoprene polymer; a first accelerator comprising at least one of a thiourea, a benzothiazole sulphenamide, a thiazole, or a dialkyl dithiocarbamate, or combinations thereof, a second accelerator comprising a thiram or a xanthogen, or a combination thereof, at least one anti-oxidant, at least one vulcanizing agent; and an activator, wherein a total amount of the first accelerator and the second accelerator ranges from 0.2 to 2.5 PHR of the polymeric, elastomeric, or latex composition and the polymeric, elastomeric, or latex composition is substantially free of diphenyl guanidine and/or casein.

Related U.S. Application Data

Provisional application No. 61/904,267, filed on Nov. 14, 2013.
START

102

STIR RESIN SOLUTION IN A TANK

104

DELIVER SULFUR DISPERSION TO TANK

106

DELIVER A STABILIZER TO THE TANK

108

HEAT THE ABOVE INGREDIENTS

110

ADD COLORANT?

112

YES

ADD COLORANT

114

NO

ADD ACCELERATOR DISPERSION

116

COOL THE MIXTURE

118

ADD SURFACANT

120

ADD ACCELERATOR

122

ADD ALKALIZED H₂O

124

ADD ANTI-OXIDANT

126

ADD AMMONIA

128

MIX FOR PERIOD OF TIME

130

END

132

FIG. 1
<table>
<thead>
<tr>
<th>COMPOSITION, PHR</th>
<th>EXAMPLE 1</th>
<th>EXAMPLE 2</th>
<th>EXAMPLE 3</th>
<th>EXAMPLE 4 (CONTROL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI LATEX</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>DITHIOCARbamate</td>
<td>0.8</td>
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<tr>
<td>XANTHOGEN</td>
<td>0.3</td>
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<tr>
<td>SULFUR</td>
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<tr>
<td>THIOUREA</td>
<td>0.2</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>THIURAM</td>
<td>0.3</td>
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<td>0.1</td>
<td>-</td>
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<tr>
<td>ANTIOXIDANT</td>
<td>3.2</td>
<td>3.2</td>
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<tr>
<td>THIAZOLE</td>
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<td>0.2</td>
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<tr>
<td>BENZOTHIAZOLE SULFENAMIDE</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
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<tr>
<td>ZnO</td>
<td>0.7</td>
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</tr>
<tr>
<td>DIPHENYL GUANIDINE</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SURFACTANT</td>
<td>1.4</td>
<td>1.4</td>
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<td>1.4</td>
</tr>
<tr>
<td>COMPOUND POT LIFE, DAYS</td>
<td>12.0</td>
<td>10.0</td>
<td>10.0</td>
<td>3.0</td>
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<tr>
<td>UNAGED ULTIMATE TENSILE STRENGTH ASTM, D412, MPA</td>
<td>21.3</td>
<td>21.5</td>
<td>23.4</td>
<td>21.0</td>
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<td>18.0</td>
<td>19.9</td>
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<tr>
<td>TEAR STRENGTH ASTM, D624, N/MM</td>
<td>27.2</td>
<td>29.5</td>
<td>32.5</td>
<td>28.9</td>
</tr>
</tbody>
</table>

1: ZINC DIETHYLDITHIOCARbamATE, ZINC DIBUTYLDITHIOCARbamATE, SODIUM DIBUTYLDITHIOCARbamATE, OR COMBINATIONS THEREOF
2: DIISOPROPYL XANTHOGEN POLYSULPHIDE, DIBUTYL XANTHOGEN POLYSULPHIDE, OR COMBINATIONS THEREOF
3: N,N'-DIPHENYL THIOUREA, N-PHENYL-N'-ALPHA-PHENYLETHYLTHIOUREA, N-PHENYL-N'-ETHYLTHIOUREA, OR COMBINATIONS THEREOF
4: DIPENTAMETHYLENE THIURAM POLYSULPHIDE, TETRABENZYL THIURAM DISULPHIDE, TETRAETHYLTHIURAM DISULPHIDE, OR COMBINATIONS THEREOF
5: METHYLMERCAPTOBENZIMIDAZOLE, BUTYLATED P-CRESOL 7 DICYCLOPENTADIENE, 2,2'-METHYLENE BIS (4-ETHYL-6-TERT-BUTYLPHENOL), OR COMBINATIONS THEREOF
6: ZINC-2-MERCAPTOBENZOTHIAZOLE, MERCAPTOBENZOTHIAZOLE, DIBENZOTHIAZYL DISULPHIDE, OR COMBINATIONS THEREOF
7: N-CYCLOHEXYL SULPHENAMIDO -2-BENZOTHIAZOLE, N-TERT-BUTYL SULPHENAMIDE -2-BENZOTHIAZOLE (TBBS), N-MORPHOLINO-THIO-2-BENZOTHIAZOLE, OR COMBINATIONS THEREOF
8: SODIUM SALTS OF NAPHTHALENESULPHONIC ACID, SODIUM LAURYL SULFATE, SODIUM LINEAR ALKYLbenzene SULFONate, OR COMBINATIONS THEREOF
9: AGED AT 70°C FOR 7 DAYS

FIG. 3
POLYMERIC COMPOSITIONS COMPRISING POLYISOPRENE

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Application Ser. No. 61/904,267, filed Nov. 14, 2013, which is incorporated by reference in its entirety.

BACKGROUND

[0002] 1. Field of the Invention

[0003] Embodiments of the present invention generally relate to polymeric compositions and articles made therefrom and, more particularly, to elastomeric articles having improved physical properties and methods of fabricating such articles.

[0004] 2. Description of the Related Art

[0005] Latex, elastomeric, or polymeric formulations are used to make flexible products having barrier properties. Such articles, for example, elastomeric articles, include condoms and gloves. Gloves are used in many industries, such as construction, industrial, and medical, as well as households, to protect the hands of users. Many such gloves comprise synthetic or natural latex or thermoplastic elastomers, such as nitrile butadiene rubber, polychloroprene, or polyurethanes.

[0006] For medical applications, such as examination and surgical gloves, gloves promote protection against germs, viruses, and microbes. Particularly for surgical gloves, it is important that the gloves have high resistance to tears, such as can be caused by tensile forces, abrasions, and the like during procedures in which scalpels, forceps, scissors, hemostats, and the like are used. However, gloves made from synthetic polyisoprene are relatively weaker than gloves made from natural rubber latex, i.e., of the Hevea brasiliensis or guayule origin, and are susceptible to breaches during use and particularly eroded use, increasing the risk of infection from doctor to patient and vice versa. As a consequence, healthcare personnel must double glove, i.e., do not use two gloves on each hand for procedures, which leads to a loss in tactile sensitivity and adds expense to surgical procedures. Moreover, wearing two gloves can tire medical personnel because of the need to overcome the stiffness of both gloves and decreases dexterity.

[0007] Also, elastomeric articles that are thin and flexible are more comfortable to users. However, the thinness and flexibility of elastomeric articles, such as gloves and condoms, comes at the expense of tear resistance properties.

[0008] Attempts to strengthen the physical properties of polyisoprene for elastomeric articles have largely failed. For example, various accelerators, have been used in rubber formulations to improve abrasion and tear-resistance. However, high levels of thioureas have strong, undesirable odors and, moreover, some of these additives, such as thioureas, diphenyl guanidine (DPG), and/or casein, which is a stabilizer, are carcinogens and/or allergens. Although DPG provides curing and scorch times that are generally longer than other accelerators, the reaction is nonetheless too quick. Additionally, the use of DPG as an accelerator and casein as a stabilizer in polymeric, elastomeric, or latex compositions is considered to have a Human Health risk characterization ratio >1 as per REACH-CLP unit. Accordingly, a casein and/or DPG-free glove is desirable for health-related concerns. Moreover, high amounts of thioureas produce malodorous compositions and are allergenic. Also, curing and scorch times, periods during which rubber compositions can be worked before curing begins, are short.

[0009] Therefore, polymeric, elastomeric, or latex compositions, which can be used to make thin, flexible elastomeric articles, having improved tensile strength, tear- and abrasion-resistance, and processes capable of producing thin, flexible elastomeric articles having improved tensile strength, as well as abrasion- and/or tear-resistance, represent an advance in the art.

SUMMARY

[0010] A glove, including a polymeric, elastomeric, or latex composition, having a water-based emulsion of a polyisoprene polymer; a first accelerator comprising at least one of a thiourea, a benzothiazole sulfenamide, a thiazole, or a dialkyl dithiocarbamate, or combinations thereof, a second accelerator comprising a thiram or a xanthogen, or a combination thereof, at least one anti-oxidant, at least one vulcanizing agent; and an activator, wherein a total amount of the first accelerator and the second accelerator ranges from 0.2 to 2.5 PHR of the polymeric, elastomeric, or latex composition and the polymeric, elastomeric, or latex composition is substantially free of diphenyl guanidine and/or casein, are disclosed and/or described in connection with at least one of the figures disclosed herein, as set forth more completely in the claims. Various advantages and features of the present invention will be more fully understood from the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only illustrative embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments. It is to be understood that elements and features of one embodiment may be in other embodiments without further recitation. It is further understood that, where possible, identical reference numerals have been used to indicate comparable elements that are common to the figures.

[0012] FIG. 1 depicts a flow diagram of a method for compounding a polymeric, elastomeric, and/or latex composition according to one or more embodiments of the invention;

[0013] FIG. 2 depicts a flow diagram of an alternate method for compounding a polymeric, elastomeric, and/or latex composition according to one or more embodiments of the invention;

[0014] FIG. 3 depicts a table showing exemplary formulations of polymeric, elastomeric, and/or latex compositions according to one or more embodiments of the invention;

[0015] FIG. 4 depicts a flow diagram of a method for producing a dipped article, such as a glove or condom, according to embodiments of the invention; and

[0016] FIG. 5 depicts a diagram for dipping a former into a polymeric coagulant solution, dipping the former into a polymeric, elastomeric, and/or latex composition, forming a coat-
ing, optionally dipping the coating into one or more coagulant solutions, and producing a glove, according to embodiments of the invention.

**DETAILED DESCRIPTION**

**[0017]** Embodiments of the present invention comprise polymeric, elastomeric, and/or latex compositions, from which elastomeric articles, such as supported gloves, unsupported gloves, and condoms, are formed. Embodiments according to the present invention further comprise methods for compounding compositions and for fabricating such articles having improved physical properties, particularly gloves and condoms, having enhanced physical properties, such as substantially enhanced unaged and aged tensile properties, as well as tear resistance. The compositions, in accordance with embodiments of the invention, comprise novel polymeric, elastomeric, and/or latex compositions that are DPG and casein free.

**[0018]** The polymeric, elastomeric, and/or latex composition comprises, for example, natural or synthetic polyisoprene. For example, synthetic, water-based polyisoprene emulsions, such as a KRAFON® IR401 formulation materials, which have a high-cis 1,4 content and a high degree of linearity, such as blends comprising polybutadiene and polystyrene. In some embodiments of the invention, the polymeric, elastomeric, or latex composition includes styrenic block copolymers of polybutadiene, and polystyrene and polyisoprene sold under the brand KRAFON®.

**[0019]** Embodiments according to the invention also comprise, for example, at least one of naturally occurring polyisoprenes, synthetic cis 1,4-polyisoprene, carboxylated acrylonitrile-butadiene, non-carboxylated acrylonitrile-butadiene, nitrile-butadiene, polychloroprene, polyvinyls butyl latex, styrene-butadiene (SBR), styrene-butadiene latex, styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene (SEBS), styrene-acrylonitrile (SAN), polyethylene-propylene-diene, water-based polyurethane, solvent-based polyurethane, or combinations or blends thereof.

**[0020]** Furthermore, natural and synthetic isoprene latexes, inherently produce flocculations, which are agglomerations of polymeric particles. The agglomeration of the particles prevents a uniform and complete vulcanization of the composition. Without intending to be bound by theory, it is believed that conventional rubber accelerators typically used in the pre-vulcanization of natural rubber and other synthetic rubber lattices, for example, DPG with casein as a stabilizer, promote the fast vulcanization of the agglomerated polymeric particles so that external portions are vulcanized while internal portions remain un-vulcanized (because once the external portions are vulcanized, sulfur or other crosslinking agents cannot penetrate the vulcanized external portions to reach the internal portions), causing a drop in overall intra- and inter-molecular crosslinking and therefore produces sub-optimal physical properties.

**[0021]** The polymeric, elastomeric, and/or latex compositions according to the invention further comprise additives, such as sulfur and zinc oxide, which provide chemical reactions for crosslinking the isoprene molecules.

**[0022]** Embodiment according to the invention further comprise polymeric, elastomeric, and/or latex compositions having at least two accelerator groups, of which a first accelerator is at least one of thioureas, thiazoles, and dialkyl dithiocarbamates, or combinations thereof; while a second accelerator comprises thiazoles and xanthogens, or combinations thereof. For example, polymeric, elastomeric, or latex compositions comprise wherein the total amount of accelerators range from 0.2% to 2.5% by weight based on dry weight of polymer (PHR, parts per hundred rubber) of which thioureas comprise between 0.2-0.4% PHR.

**[0023]** Dialkyl dithiocarbamates according to the invention comprise sodium dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc diethyl dithiocarbamate, zinc dibutyldithiocarbamate, sodium diethyldithiocarbamate, sodium dibutyldithiocarbamate, zinc dibenzyl dithiocarbamate and combinations thereof.

**[0024]** Thiazoles according to the invention comprise tetramethyl thiuram disulfide, tetraethyl thiuram disulfide, tetraetyl thiuram disulfide, dipentamethylene thiuram disulfide and combinations thereof.

**[0025]** Xanthogens according to the invention comprise diisopropyl xanthophenyl polysulfide, dihydrocarbaryl xanthogen polysulfide, dibutyl xanthogen polysulfide, and combinations thereof.

**[0026]** Thiazoles according to the invention comprise mercapto benzothiazole, mercapto benzothiazole, dibenzothiazyl disulfide, N-cyclohexyl sulphanamido-2-benzothiazole, N-tert-butyl sulphanamide-2-benzothiazole (TBBS), N-morpholino-thio-2-benzothiazole, and combinations thereof.

**[0027]** Thioureas according to the invention comprise N,N'-diphenyl thiourea (DPTU), N-phenyl-N-cyclohexyl thiourea, N-phenyl-N-alpha-phenylethyl thiourea. N-phenyl-N'-ethyliothione, N-para-methoxyphenyl N'-ethyliothione, and combinations thereof.

**[0028]** The use of low amounts of a thiazole and a thiourea accelerator in combination in polymeric, elastomeric, and/or latex compositions provides a particularly long shelf life time. In this context, a low amount means wherein the total amount of accelerators range from 0.2% to 2.5% PHR. Also, a comparatively longer composition pot life is possible when DPG, with milk casein as a stabilizer, is not used, thereby increasing the operating window of the composition during processing to manufacture elastomeric articles therewith.

**[0029]** Without intending to be limited by the theory or mechanism of operation, it is believed that the novel use of a thiazole and a thiourea accelerator in combination in low amounts, for example, TBBS and DPTU, slows the pre-curing and vulcanization reaction rates to a level unrealized with previous accelerator combinations, i.e., longer shelf times. Moreover, because the vulcanization is so slowed, a range of polymeric, elastomeric, or latex composition temperatures may be employed. This range of temperatures, such as approximately 20° C. to 35° C., allows the crosslink density to be optionally varied, as needed, to impart different desired physical properties, thereby allowing various compositions to be “tuned” for different service applications. Because the amount of crosslink density can be varied, i.e., physical properties, such as tear resistance, as well as substantially enhanced unaged and aged tensile strength, of the resulting article, e.g., a surgical glove, examination glove, supported glove, condom, or the like, are now possible. It is believed, without being bound by theory, that because DPTU and TBBS slows the vulcanization, longer polysulfide (polysulfide) bonding is created, resulting in higher tensile strength at relatively low crosslink densities.

**[0030]** It is further believed that the film architecture of a polymeric, elastomeric, or latex film, vulcanized using sulfur as a crosslinking agent, is made of sulfur cross links occurring
between the polymer molecules within the particles (intra-
molecular) as well as between the particles (inter-
molecular) due to the mobility of polymeric chains. This results in a
partially pre-vulcanized film or coating, which may be
formed on a mold, for example, a ceramic mold, i.e., alumi-
nosilicates, glasses, etc., in the shape of a glove or condom,
which is dipped into a polymeric, elastomeric, or latex com-
position. Embodiments according to the invention comprise
pre-vulcanizing the polymeric, elastomeric, or latex composi-
tion at a range of 20°C to 35°C. to achieve an acceptable degree
of crosslinking, which, in some embodiments according to
the invention, requires between 10 and 20 hours. In at least
one exemplary embodiment, approximately 20 hours is
appropriate.

[0031] The film or coating disposed on the mold is post-
vulcanized in, for example, an oven ranging in temperature
from approximately 110°C. to 130°C. The nature of cross
links (short chain mono-, and di- and long-chain polysulphide
links) as well as types of cross links that form between
particles by control, for example, shear control, of degree of
pre-vulcanization in polymeric, elastomeric, or latex composi-
tion and post processing conditions dictates the film archi-
tecture.

[0032] Moreover, it is believed that the use of TBBS and
DPTU, which provides a long shelf time, as discussed
above, also mitigates the vulcanization of the outer portions
of polymeric, elastomeric, or latex flocculations (also known
as peripheral crosslinking), and thereby promotes the vulca-
nization of the inner portions of the flocculations, providing a
stronger polymeric structure. Furthermore, it is believed that
the use of TBBS and DPTU promotes crosslinking while the
polymeric, elastomeric, or latex composition ages, resulting
in further increases in tensile strength, as opposed to the use
of other accelerators, such as DPG, which exhibit a drop in
tensile strength during aging. Even further, polymeric, elas-
tomeric, or latex compositions comprising between approxi-
mately 0.2 PHR to approximately 2.5 PHR total of a thiazole
accelerator and a thiourea accelerator are substantially less
malodorous. And, as discussed above, such compositions are
also substantially more allergenic. FIG. 3 depicts composi-
tions, reciting ranges of amounts of various ingredients,
according to embodiments of the invention, for several exam-
plary polymeric, elastomeric, and/or latex compositions con-
prising various amounts of thiocarbamates, xanthogens,
thioureas, thiuramdis, and/or thioazoles, and the physical data
associated therewith compared with a control composition.
The polymeric, elastomeric, and/or latex compositions may
be compounded as discussed below.

[0033] As can be seen in FIG. 3, the DPG-free and casein-
free embodiments of the invention have surprisingly
enhanced ultimate tensile strengths (UTS) and tear strengths.
Moreover, the pot life of each example is also significantly
longer than the control. At least one exemplary embodiment
of the invention includes a polymeric, elastomeric, or latex
composition capable of producing an article having an
unaged UTS of at least 20 MPa and aged ultimate tensile
strength strength of at least 18 MPa after accelerated aging at 70°C.
for 7 days, and a tear strength of 25 N/mm.

[0034] The polymeric compositions in FIG. 3 generally
have viscosities ranging from 250-5000 centipoise and com-
prise commonly used stabilizers including but not limited to
potassium hydroxide, ammonia, sulfonates, and the like. The
composition may contain other commonly used ingredients
such as surfactants, anti-microbial agents, fillers/additives,
pigments, and the like. At least one embodiment of the inven-
tion disclosed herein includes a composition comprising fill-
ers and/or reinforcements, such as silica, metallic and
ceramic powders, glass-fibers, and the like to provide grip,
texture, strength, and other physical properties. Such fillers
and reinforcements can, for example, comprise between 2-20%
of a material by weight. In other embodiments, fillers
and reinforcements may comprise between 20-50% by
weight for various applications tailored to end properties.
Other additives are optionally added as needed, such as for
flame-, heat-, and arc- retardance, adhesion promoters, ultra-
 violet stabilization, hardness, pigments, and the like.

[0035] In some embodiments of the invention, the poly-
meric, elastomeric, and/or latex compositions are foamed, so
that air cells dispersed in the range of 5-50 volumetric per-
centage are formed. When a composition is disposed on a
former as a coating, closed cells or open cells may be formed,
as is described in commonly-assigned U.S. Pat. Nos. 8,192,
834, 8,001,809, and 7,814,571, which are herein incorporated
by reference in their entirety. In some embodiments of the
invention, the cells are interconnected in the polymeric latex
layer. Closed cells provide a liquid proof polymeric latex
coating that is highly flexible, soft and spongy, and provides
good dry and wet grip. Closed cells, generally, have air con-
tent ranging from 5-15 volumetric percent. Open cells, which
are interconnected, generally range from approximately
15-50 volumetric percentage range and provide a breathable
article, i.e., a glove, through the foamed polymeric latex layer.
This foamed polymeric latex layer may penetrate half or more
of the thickness of the knitted liner, though the polymeric
latex layer does not penetrate the entire thickness, thereby
substantially avoiding strike-through, i.e., skin contact with
the polymeric latex.

[0036] The polymeric composition may contain additional
surfactants such as TWEEEN® 20 to stabilize the latex foam.
Once the composition is foamed with appropriate air content
and the viscosity is adjusted, refinement of the foam is under-
taken by using an impeller at a suitable speed as is known to
those in the art. Air bubble size may be refined using a differ-
ent impeller at a reduced speed. The elastomeric coating,
irrespective of whether foamed, may be applied by dipping a
former, or a former having a knitted liner dressed thereon, into
a latex emulsion or spraying the coating onto the liner or, for
unsupported gloves, dipping the former directly into the latex
emulsion or spraying the former with the latex emulsion.

[0037] A process for making a dipped article, in accordance
with embodiments of the invention as discussed below, com-
prises the steps of dipping the former into a coagulant, for
example, a strong coagulant, such as calcium nitrate, dipping
the former into the polymeric, elastomeric, or latex composi-
tion to form a dipped article, such as a surgical or examina-
tion glove or condom. In some embodiments of the invention,
the former is dipped into a weak coagulant, such as a weak
acid, such as an aqueous solution of acetic acid or formic acid.
The article may then be optionally dipped into a strong coagu-
lagant. Without intending to be bound or limited by theory, it is
believed that strong coagulants acting on the outer layers
promote the fast gelling of the outer layers, resulting in a
case-hardening. A solidified outer surface prevents the coagu-
lant from migrating into the interior of the layer of the film or
coating, resulting in the incomplete gelling of the interior. In
other words, strong coagulant's acting on the outer layer of the
film or coating promote the fast gelling of the outer layers,
thereby not allowing the coagulant to reach the interior.
Therefore, gelling of the interior of, for example, a coating is incomplete. Alternatively, a weak acid promotes the gelling of the interior of film or coating, because a weak acid slowly gels the exterior surface and migrates slowly into the interior of the latex layer, resulting in slower and complete gelling. After dipping in a weak acid, optionally dipping the article into a strong coagulant hardens the exterior surface.

[0038] It is further believed that where the interior of the article is allowed to more completely gel, the polymeric molecules get closer and, for example, zinc, zinc oxide, or sulfur crosslinks are enhanced. It is believed that an increase in crosslinking results in significant and unexpected increases in abrasion resistance. As discussed above, in some embodiments of the invention, the application of the weak acid is followed by the application of a strong coagulant, such as 2-15 wt % calcium nitrate aqueous coagulant solution.

[0039] The coagulant solution, which destabilizes and coagulates a polymeric, elastomeric, or latex composition, comprises one or more of calcium nitrate, calcium chloride, sodium chloride, potassium chloride, aluminum chloride, aluminum sulfate, and like salts. These coagulants are highly soluble in water and are strong coagulants. Also, water-based, polymeric, coagulant coatings, for coating the former, capable of producing a thickness in the range of about 5 to 50 micrometers on a former, may be used in embodiments of the invention. The polymeric coagulant coating solution possesses adequate former surface-wetting properties and sufficient viscosity or rheology characteristics so as to form a thin layer of polymeric coagulant coating. At least one way to accomplish this is by adding wetting agents and viscosity modifiers to the polymeric coagulant coating solution.

[0040] The polymeric coagulant coating dries at a reasonable rate, providing a well-defined operating time period, during which the polymeric coagulant coating remains tacky to accept the application of discrete coagulant particles defining the size, shape and distribution of the desired geometrical texture of the glove surface. One exemplary polymeric coagulant coating solution includes polymers selected from poly N-vinyl-2-pyrrolidone (PVP), polyvinyl alcohol (PVA), polycrylic acids (PAA), polyacrylamide (PAC), and/or a copolymer or derivative of PVP, PVA, PAA or PAC. The amount of polymer present is in the range of approximately 0.1 to 10 dry weight percent, and in some embodiments of the invention, the amount of polymer present is in the range of approximately 1 to 7 dry weight percent, as is described in commonly-assigned U.S. Pat. No. 7,814,570, which is herein incorporated by reference in its entirety.

[0041] FIG. 1 depicts a flow diagram of a method 100 for compounding a polymeric, elastomeric, or latex composition according to one or more embodiments of the invention. The method 100 starts at step 102 and proceeds to step 104, at which point a solution of polysiloxane, for example, a KRA-TON®, polysiloxane latex, for example, a KRA-TON® IR-401B, is stirred in a tank. At step 106, a sulfur dispersion, optionally while the tank is still stirring, is stirred into the tank for a suitable time. At step 108, a stabilizer is mixed therein for approximately one hour. The method 100 proceeds to step 110, at which point the contents of the tank, the polysiloxane latex, sulfur, and stabilizer are heated for approximately thirty minutes.

[0042] At step 112, optionally, a decision as to whether to add a colorant is made, such as titanium dioxide, which is added at step 114. The method 100 then proceeds to step 116, at which point one or more accelerators is added, for example, a thiazole and a thiourea. In at least one embodiment according to the invention, the thiazole comprises TBBS and the thiourea comprises DPTU, and may further comprise a dithiocarbamate, such as dipentamethylene thirametrarsulfide (DPTT), which are added to the tank and mixed. At step 118, optionally, the above mixture is cooled to, for example, 28-32°C. At step 120, a surfactant is optionally introduced into the mixture. At step 122, optionally, another accelerator, for example, a dithiocarbamate, such as zine diethyl dithiocarbamate (ZDEC), is mixed into the tank. At step 124, optionally, an alkalized chilled water is mixed into the mixture. At step 126, an antioxidant is mixed in and at step 128, a solution of ammonium hydroxide is mixed into the tank. At step 130, the mixture is mixed for a period of time. At step 132, the method 100 ends.

[0043] FIG. 2 depicts a flow diagram of an alternate method 200 for compounding a polymeric, elastomeric, and/or latex composition according to one or more embodiments of the invention. At least one exemplary method for compounding the compositions shown in FIG. 3 is the following. The method 200 starts at step 202. An amount of a DPG-free and casein-free polymer, such as a polymer comprising polyisoprene, for example, KRATON® IR-401B polymer/latex is delivered to a mixing tank and stirred with a sulfur dispersion at step 204 for approximately 30 minutes and proceeds to step 206 at which point a stabilizer solution is stirred therein. At step 208, the mixture may be heated for an appropriate amount of time and allowed to compound or mature for approximately one hour, after which an appropriate amount of an accelerator, such as a thiram dispersion, is stirred at step 210. At step 212, an activator is stirred into the mixture. At step 214, an anti-oxidant is stirred into the mixture. At step 214, the method 200 ends.

[0044] At least one exemplary method for compounding the compositions shown in FIG. 4 is the following. An amount of isoprene, for example, KRATON® IR-401B polymer/latex is delivered to a mixing tank and stirred. A sulfur dispersion is added to the tank and stirred for approximately 30 minutes and a stabilizer solution is introduced. This composition is allowed to compound for approximately one hour and an appropriate amount of a thiram dispersion is introduced along with a titanium dioxide dispersion. The composition is allowed to compound for approximately one hour. For approximately 12-60 hours, the composition is allowed to mature, stirring at 30 minute intervals.

[0045] In at least one embodiment according to the invention, an appropriate amount of dithiocarbamate, such as at least one of sodium dibutyl dithiocarbamate, such as 5% Butyl Nanate® or zinc diethyl dithiocarbamate, followed by a xanthogen polysulphide, such as ROBAC AS100, is introduced into the mixing tank. Chilled alkalized water is optionally added to the mixing tank. An antioxidant methylmercapto-benzimidazole dispersion of soft water and ammonia is mixed slowly when the temperature of the composition drops to approximately 22°C. An appropriate amount of a titanium dioxide dispersion, for example, Ralox LC, a potassium caprylate, e.g., Alkylon 8627, and/or styrene/maleic anhydride copolymer, esterified with a low molecular weight sec. butyl ester, e.g., Scriptap 550 5% solution is introduced to the mixing tank and stirred.

[0046] FIG. 4 depicts a flow diagram of a method 300 for producing a dipped article, such as a glove or condom, according to embodiments of the invention. In some embodiments, each and every step of the method 300 is performed. In other embodiments, some steps are omitted or skipped.
Method 300 starts at step 301 and proceeds to step 302, at which point a decision is made whether to pre-heat the former. If the answer is yes, the former is heated, for example, to 50-60°C, at step 303. If the answer is no, the method 300 proceeds directly to step 304, at which point the former, such as a glass or ceramic former, is dipped into a tank having a coagulant. At step 306, the former is removed from the tank, dried for approximately 1-5 minutes at, for example, 30-60°C. At step 308, and dipped into a tank having a polymeric, elastomeric or latex composition, as described above, and a coating forms on the former in the shape of an article.

At process step 310, the former having a first elastomeric coating disposed thereon is dipped into a tank having a coagulant, for example, an aqueous solution containing a strong or weak acid for a few seconds to several minutes. In some embodiments of the invention, the weak acid is a solution of acetic acid. At process step 312, the former having the coating disposed thereon is optionally dipped into a strong coagulant such as calcium citrate, calcium nitrate, or another coagulant as is known by those in the art, and removed. At process step 314, it is determined whether to add a second coating of onto the first elastomeric coating. If the answer is yes, the method 300 returns to step 308. Also, either the first of second coating may be foamed or unfoamed, irrespective of whether the first layer is foamed or unfoamed, and vice versa. If no second coating is to be added, the method 300 proceeds to process step 316. At step 316, the glove is optionally leached of impurities and proteins, for example, in an aqueous solution 35-50°C for approximately 1-3 minutes. At process step 318, the glove is allowed to dry in air. At process step 320, the glove is placed in an oven for curing, for example, at 80-100°C, for 30 to 40 minutes. At process step 322, the method 300 ends.

FIG. 5 depicts a diagram 500 for dipping a former into a polymeric coagulant solution, dipping the former into a polymeric, elastomeric, and/or latex composition, forming a coating, optionally dipping the coating into one or more coagulant solutions, and producing a glove, according to embodiments of the invention. In FIG. 5, there is shown generally a diagrammatic representation of a processing line in which a tank 506, in which a former 504, such as a hand shaped former, is dipped, forming a polymeric coagulant coating 502 on the former 504. The former 504 having the polymeric coagulant coating 502 disposed thereon is removed from the tank 506. The former 504 having the polymeric coagulant coating 502 disposed thereon is optionally allowed to dry and subsequently dipped in a polymeric, elastomeric, and/or latex composition 510 in a tank 512, forming a coating of composition 510 thereon. The former 504 is subsequently delivered to a tank 516 containing a coagulant solution 518, for example, a weak coagulant, such as acetic acid, formic acid, or the like, which promotes a slow gelling of the coating of composition 510. The coagulant solution 518 on the coating of composition 510 on the former 504 is optionally allowed to dry and is dipped into a tank 524 containing a strong coagulant 522, such as calcium nitrate, as discussed herein. The former 504 having the above disposed thereon is then optionally allowed to dry and dipped into a tank 528 containing a polymeric, elastomeric, and/or latex composition 526, which may be the same or a different polymeric, elastomeric, and/or latex composition than in tank 512 or, may be, for example, a foamed composition. A water wash station (not shown) may leach impurities for the polymeric, elastomeric, and/or latex composition. A heating station (not shown), for example, an oven, cures the polymeric, elastomeric, and/or latex coating(s) disposed on the former 504 to form a glove 530. A stripping station (not shown), strips the glove is stripped from the former 504 and optionally inverts the glove 530.

The use of the terms “a” and “an” and “the” and other references describing embodiments of the invention are to be construed both in the singular and plural unless otherwise indicated or clearly contradicted by context. Ranges of values herein are merely intended to serve as a shorthand method of referring to each separate value falling within the range; unless otherwise indicated herein, and each range value is incorporated into the specification as if individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illustrate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention. While the invention is described herein by way of example using several embodiments and illustrative drawings, those skilled in the art will recognize that the invention is not limited to the embodiments of drawing or drawings described.

The headings used herein are for organizational purposes only and are not meant to be used to limit the scope of the description or the claims. As used throughout this application, the word “may” is used in a permissive sense (i.e., meaning having the potential to), rather than the mandatory sense (i.e., meaning must). Similarly, the words “include,” “including,” and “includes” mean including, but not limited to. The word “glove” means glove or glove liner. The terms dispersion, emulsion, and composition may also be used interchangeably herein.

All ranges recited herein include values therebetween and can be inclusive or exclusive of the endpoints. Optional included ranges are from integer values therebetween (or inclusive of one original endpoint), at the order of magnitude recited or the next smaller order of magnitude. For example, if the lower range value is 0.2, optional included endpoints can be 0.3, 0.4, … 0.1, 1.2, and the like, as well as 1, 2, 3 and the like; if the higher range value is 8, optional included endpoints can be 7, 6, and the like, as well as 7.9, 7.8, and the like. One-sided boundaries, such as 3 or more, similarly include consistent boundaries (or ranges) starting at integer values at the recited order of magnitude or one lower. For example, 3 or more includes 4 or more, or 3.1 or more.

Although a few exemplary embodiments of the invention have been described in detail above, those skilled in the art will appreciate that many modifications are possible in embodiments without materially departing from the teachings disclosed herein. Any and all such modifications are intended to be included within the embodiments of the invention, and other embodiments may be devised without departing from the scope thereof, and the scope thereof is determined by the following claims. Therefore, it should be understood that the drawings and detailed description therefor are not intended to limit the invention to the particular form disclosed, but on the contrary, the invention is to cover all equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.
What is claimed is:

1. A glove, comprising:
   a polymeric, elastomeric, or latex composition, comprising:
   a water-based emulsion of a polyisoprene polymer;
   a first accelerator comprising at least one of a thiourea, a
   benzothiazole sulphenamide, a thiazole, or a dialkyl
dithiocarbamate, or combinations thereof;
   a second accelerator comprising a thiram or a xantho-
gen, or a combination thereof;
   at least one anti-oxidant;
   at least one vulcanizing agent; and
   an activator;
   wherein a total amount of the first accelerator and the
   second accelerator ranges from 0.2 to 2.5 PPHR for the
   polymeric, elastomeric, or latex composition and the
   polymeric, elastomeric, or latex composition is sub-
   stantially free of diphenyl guanidine and/or casein.

2. The glove of claim 1, wherein the glove is a powder-free
   glove.

3. The glove of claim 1, wherein the dialkyl dithiocarbamate
   is at least one of sodium dimethyldithiocarbamate, zinc
   dimethylidithiocarbamate, zinc diethyl dithiocarbamate, zinc
dibutyl dithiocarbamate, sodium diethylidithiocarbamate,
sodium dibutyl dithiocarbamate, zinc dibenzylidithiocarbamate
   or combinations thereof.

4. The glove of claim 1, wherein the thiram is at least one of
   tetramethyl thiuram disulphide, tetraethyl thiuram disulphide,
tetramethyl thiuramtrisulphide, dipentamethylene thiuramtris-
sulphide or combinations thereof.

5. The glove of claim 1, wherein the xanthogen is diiso-
   propyl xanthogen polyisulfide, dihydrocarbaryl xanthogen
   polyisulfide, dibutyl xanthogen polyisulfide, or combinations
   thereof.

6. The glove of claim 1, wherein the thiazole is mercapto-
   benzothiazole, mercapto benzothiazole, dibenzothiazyl
   disulphide, or combinations thereof.

7. The glove of claim 1, wherein the benzothiazole sulphe-
   namide is N-cyclohexyl sulphenamide-2-benzothiazole,
   N-tert-butyl sulphenamide-2-benzothiazole (TBBS), N-mor-
   pholinio-thio-2-benzothiazole, or combinations thereof.

8. The glove of claim 1, wherein the thio urea is N,N'-
   diphenyl thiourea (DPTU), N-phenyl-N-cyclohexyl thiourea,
   N-phenyl-N-alpha phenylethyliourea, N-phenyl-N'-eth-
   ylthiourea, N-para-methoxyphenyl N'-ethylthiourea, or combi-
   nations thereof.

9. The glove of claim 1, wherein comprising a natural poly-
   isoprene, a synthetic cis 1,4-polyisoprene, a carboxylated
   acrylonitrile butadiene, a non-carboxylated acrylonitrile
   butadiene, a nitrile-butadiene, a polychloroprene, polyvinyls,
   a butyl latex, a styrene-butadiene (SBR), a styrene-butadiene
   latex, a styrene-isoprene-styrene (SIS), a styrene-ethylene/
   butylene-styrene (SEBS), a styrene-acrylonitrile (SAN), a
   polyethylene-propylene-diene, a water-based polyurethane,
   a solvent-based polyurethane, or blends thereof.

10. The glove of claim 1, wherein the polymeric, elastomeric,
    or latex composition comprises approximately 0.2
    PPHR DPTU and approximately 0.2 to 0.4 PPHR TBBS.

11. The glove of claim 2 wherein at least one glove,
    coating for a glove, or condom has an unaged ultimate tensile
    strength of at least 20 MPa and/or aged ultimate tensile
    strength of at least 18 MPa after accelerated aging at 70° C.
    for 7 days, and a minimum tear strength of 25 N/mm.

12. A method for compounding a polymeric, elastomeric,
    or latex composition substantially free of diphenyl guanidine
    and casein, comprising:
    stirring a polyisoprene material and sulfur to form a mixture;
    stirring a stabilizer into the mixture;
    heating the stabilizer and mixture;
    stirring an accelerator mixture comprising between 0.2
    PPHR to approximately 2.5 PPHR total of the polymeric,
    elastomeric, or latex composition into the mixture;
    stirring an activator into the mixture; and
    stirring an anti-oxidant in the mixture, wherein a poly-
    meric, elastomeric, or latex composition substantially free
    of diphenyl guanidine and casein is formed.

13. The method of claim 12, further comprising a step for
    delivering a thiram accelerator into the diphenyl guanidine
    free and casein free polymeric, elastomeric, or latex com-
    position.

14. A method for making a polymeric, elastomeric, or latex
    article, comprising:
    dipping a former into a coagulant;
    dipping the former into a polymeric, elastomeric, or latex
    composition, thereby disposing a polymeric, elastomeric,
    or latex coating onto the former;
    dipping the polymeric, elastomeric, or latex coating into at
    least one of a weak acid or a strong coagulant; and
    allowing the polymeric, elastomeric, or latex coating to
dry, wherein the former is a hand shaped former or a
    condom former, thereby forming a powder-free unsup-
    ported glove or condom.

15. The method of claim 14, wherein the polymeric, elastomeric,
    or latex composition further comprises a natural
    polyisoprene, a synthetic cis 1,4-polyisoprene, a carboxy-
    lated acrylonitrile butadiene, a non-carboxylated acrylon-
    trile butadiene, a nitrile-butadiene, a polychloroprene, poly-
    vinyls, a butyl latex, a styrene-butadiene (SBR), a styrene-
    butadiene latex, a styrene-isoprene-styrene (SIS), a styrene-
    ethylene/butylene-styrene (SEBS), a styrene-acrylonitrile
    (SAN), a polyethylene-propylene-diene, a water-based poly-
    urethane, a solvent-based polyurethane, or combinations or
    blends thereof.

16. The method of claim 14, wherein the former is heated
    before the dipping step.

17. The method of claim 14, further comprising a step of
    pre-vulcanizing the polymeric, elastomeric, or latex com-
    position at a range of 20°-35° C. and achieving a required degree
    of crosslinking not faster than approximately 20 hours.

18. The method of claim 14, further comprising a step of
    post-vulcanizing the powder-free unsupported glove or
    condom at a temperature range of 110°-150° C.

19. The method of claim 14, further comprising a step for
    foaming the polymeric, elastomeric, or latex composition
    before the dipping the former into a polymeric, elastomeric,
    or latex composition.

20. The method of claim 14, further comprising a step for
    dressing the former with a fabric liner before the dipping
    the former into a polymeric, elastomeric, or latex composition
    step, wherein the composition is thereby disposed on the
    fabric liner to form a supported article.