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(54) Title: COMPOSITIONS CONTAINING COPOLYMERS OF ISOPRENE, BUTADIENE AND/OR STYRENE FOR USE IN HUMAN SKIN CARE AND HAIR CARE

(57) Abstract: The invention provides personal care compositions which include polymers of isoprene, butadiene and/or styrene, particularly conjugated dienes which may be subject to some degree of hydrogenation. A copolymer of two different conjugated dienes is preferred. The polymers may be selectively hydrogenated to produce polymers which have highly controlled amounts of unsaturation, thereby improving film forming properties.



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**COMPOSITIONS CONTAINING COPOLYMERS
OF ISOPRENE, BUTADIENE AND/OR STYRENE FOR
USE IN HUMAN SKIN CARE AND HAIR CARE**

5 **CROSS- REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Patent Application No. 60/158,509, filed October 8, 1999. This application is also related by subject matter to U.S. Application Serial No. 09/429,947, filed October 29, 1999.

10

BACKGROUND OF THE INVENTION

This invention is directed to personal care formulations comprising copolymers of isoprene, butadiene and or styrene which have improved film forming properties. More particularly, this invention is directed to personal care formulations comprising liquid block copolymers having unsaturation only on the terminal blocks and methods of preparation thereof for use in personal care.

15 Polymeric materials are used in a variety of skin and hair care products. Various oxygen and nitrogen containing polymers, e.g., polyacrylates, polymethacrylates, polyethers, alkylacrylamide copolymers, etc, are generally used. Hydrocarbon polymers are less frequently used and generally consist of various grades of polyisobutylene (PIB). This latter group is employed because polymers of this class are quite compatible with hair and skin as a result of their oleaginous nature, i.e., they spread out smoothly on the desired surface and impart a desirable surface quality. The primary difficulty associated with low molecular weight PIB's is their tendency to be removed during use with ease, thus decreasing their utility.

25 Emollients including organic esters and hydrocarbons, especially petrolatum, have long been used medicinally as skin conditioning agents. These substances are second only to water as moisturizing ingredients of choice. They function primarily

as an occlusive barrier. The water content of the outer layers of human skin, stratum corneum, is a controlling factor in the appearance of dry skin symptoms. When the stratum corneum contains an adequate amount of water within the range of 10 to 20%, the skin remains flexible. However, when the water content falls below 10%
5 the stratum corneum often becomes brittle and rough and can exhibit scaling and cracking.

Where improved protective qualities, high water resistance, and substantive barrier characteristics are desired, it is customary in the art to incorporate various organic waxes and resins into the product in order to achieve these goals. What has
10 been discovered in accordance with the present invention is that certain diene/arene copolymers can be employed as viable alternatives to the customary materials (organic waxes and resins) in personal care formulations.

Therefore, it is the object of the present invention to provide new polymers for personal care formulations with improved properties.

15 Further, it is the object of the present invention to provide new polymers for personal care formulations with improved conditioning properties.

In particular, it is the object of the present invention to improve the properties of human hair and skin care products by the use of low molecular weight hydrocarbon polymers prepared from isoprene, butadiene and/or styrene because of
20 the variety of unique properties they possess.

SUMMARY OF THE INVENTION

The present invention is useful for all types of personal care or cosmetic
25 compositions for topical treatment of or application to human hair or skin including but not limited to hand, facial and scalp cleansers, shampoos, antiperspirants, deodorants, skin conditioners, night creams, moisturizers, refreshers, softeners, wrinkle, itch blemish and acne reducers and inhibitors, sunscreens, insect repellants, topical analgesics, antiseptics and wound protectants, shave and aftershave

preparations, hair conditioners, colorants, rinses, and fixatives, foam baths, bodywash and the like.

Selectively hydrogenated low molecular weight polymers based on isoprene, butadiene and styrene are inherently immiscible in water and soluble in a wide range of organic materials including hydrocarbon and ester fluids. These polymers are
5 useful in the preparation of personal care formulations containing complex mixtures of ingredients and lead to enhanced performance of active ingredients.

Hydrocarbon polymers of the present invention, having a molecular weight of 2,000 to 100,000, offer the possibility of a level of viscosity control and range that is
10 not available to other technologies. Additionally, the particular arrangement of specific monomer blocks within the polymer allow for additional manipulation of bulk polymer properties useful to final performance, e.g., linear vs star-branched structures. Further, selective hydrogenation of the subject polymers provides for a further level of product control not available to other technologies, including, but not
15 limited to a high degree of product stability, an enhanced level of bulk viscosity manipulation through control of crystallinity, and control of index of refraction.

Some personal care formulations rely on the presence of UV absorbers (typically organic compounds) in a mixture of organic and aqueous components. Because of the miscibility of many of the formulation components with water, UV
20 protection may be diminished as a result of reintroduction of water following personal care application. This reintroduction may occur by any of several means, but two primary routes are by swimming and perspiration.

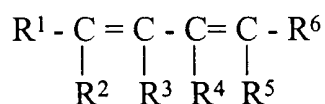
It is believed that the introduction of a non-aqueous, water-insoluble component to the personal care formulation would extend the effectiveness of the UV
25 absorbers by preventing the removal upon the reintroduction of water.

The non-aqueous water-insoluble component of the present invention are polymers and copolymers of isoprene, butadiene and/or styrene. Selectively hydrogenated isoprene-butadiene copolymers are preferred. The copolymers of the present invention, while providing no UV protection, have the additional advantage

of being non-toxic and non-tacky when applied to skin. A choice of UV absorber may be suggested based on its solubility in the different formulation phases containing the copolymers of the present invention.

The invention provides personal care formulations which include polymers of conjugated dienes which may be partially, selectively or completely hydrogenated. In one embodiment of the invention, there is provided a personal care formulation comprising a copolymer of two different conjugated dienes. In this case, the first conjugated diene includes at least one relatively more substituted conjugated diene having at least five carbon atoms and the formula:

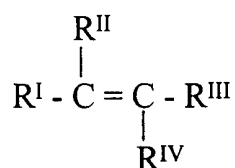
(1)



wherein R^1 - R^6 are each hydrogen or a hydrocarbyl group, provided that at least one of R^1 - R^6 is a hydrocarbyl group, and also provided that, after polymerization, the unsaturation of the polymerized conjugated diene of formula (1) has the formula:

(2)

20



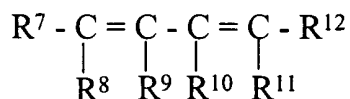
wherein R^I , R^{II} , R^{III} and R^{IV} are each hydrogen or a hydrocarbyl group, provided that either both R^I and R^{II} are hydrocarbyl groups or both R^{III} and R^{IV} are hydrocarbyl groups.

The second conjugated diene in the personal care formulation of this embodiment includes at least one relatively less substituted conjugated diene which is

different from the first conjugated diene and has at least four carbon atoms and the formula:

(3)

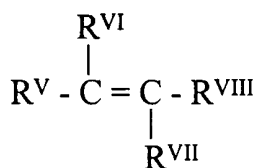
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wherein R^7 - R^{12} are each hydrogen or a hydrocarbyl group, provided that, after
10 polymerization, the unsaturation of the polymerized conjugated diene of formula (3) has the formula:

(4)

15

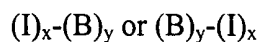


wherein R^V , R^{VI} , R^{VII} and R^{VIII} are each hydrogen or a hydrocarbyl group, provided that one of R^V or R^{VI} is hydrogen, one of R^{VII} or R^{VIII} is hydrogen, and at least one of R^V , R^{VI} , R^{VII} and R^{VIII} is a hydrocarbyl group.

20 Following polymerization, the diene copolymer may be partially, selectively or completely hydrogenated.

In a preferred embodiment, the personal care formulation includes a polymer in which the first and second conjugated dienes are polymerized as a block copolymer including at least two alternating blocks:

25



In this case, the block (I) includes at least one polymerized conjugated diene of formula (1), while the block (B) includes at least one polymerized conjugated diene of formula (3). In additions, x is the number of polymerized monomer units in block (I) and is at least 1, and y is the number of polymerized monomer units in block (B) and is at least 25. It should be understood throughout that x and y are defined relative to blocks in a linear block copolymer or blocks in an arm or segment of a branched or star-branched copolymer in which the arm or segment has substantially linear structure.

Preferably, in the block copolymers of this embodiment, x is at least about 1 and at most about 600, preferably at most about 300; and y is at least about 30 and at most about 2,000, preferably at most about 1,500. While larger values for x and y are generally related to larger molecular weights, polymers which have multiple blocks and star-branched polymers typically will have molecular weights which are not well represented in the values of x and y for each block.

Alternatively, the personal care formulation includes the first and second conjugated dienes polymerized as a random copolymer. The personal care formulation may also include the first and second conjugated dienes polymerized as a branched or star-branched copolymer.

The copolymers useful according to this embodiment generally have a molecular weight of at least about 2,000, preferably at least about 3,000, and more preferably at least about 5,000. The molecular weight of these polymers is at most about 100,000, preferably at most about 50,000, and more preferably at most about 35,000.

In the personal care formulations of the invention, the copolymer is preferably selectively hydrogenated. It is preferred that the unsaturation of formula (4) be substantially completely hydrogenated, thereby retaining substantially none of the original unsaturation of this type, while the unsaturation of formula (2) is substantially retained (i.e., the residual unsaturation after hydrogenation).

After the hydrogenation reaction, the Iodine Number for the residual unsaturation of formula (2) is generally from about 50% to about 100% of the Iodine Number prior to the hydrogenation reaction. More preferably, after hydrogenation, the Iodine Number for the residual unsaturation of formula (2) is about 100% of the Iodine Number prior to the hydrogenation reaction.

After the hydrogenation reaction, the Iodine Number for the residual unsaturation of formula (4) is from about 0% to about 10% of the Iodine Number prior to the hydrogenation reaction. More preferably, after the hydrogenation reaction, the Iodine Number for the residual unsaturation of formula (4) is from about 0% to about 0.5% of the Iodine Number prior to the hydrogenation reaction. Most preferably, after the hydrogenation reaction, the Iodine Number for the residual unsaturation of formula (4) is from about 0% to about 0.2% of the Iodine Number prior to the hydrogenation reaction.

The conjugated diene of formula (1) preferably includes a conjugated diene such as isoprene, 2,3-dimethyl-butadiene, 2-methyl-1,3-pentadiene, myrcene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, 2-phenyl-1,3-pentadiene, 3-phenyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-hexyl-1,3-butadiene, 3-methyl-1,3-hexadiene, 2-benzyl-1,3-butadiene, 2-p-tolyl-1,3-butadiene, or mixtures thereof. More preferably, the conjugated diene of formula (1) includes isoprene, myrcene, 2,3-dimethyl-butadiene or 2-methyl-1,3-pentadiene. Still more preferably, the conjugated diene of formula (1) includes isoprene.

Preferably, the conjugated diene of formula (3) includes 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2,4-heptadiene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3-nonadiene, 2,4-nonadiene, 3,5-nonadiene, 1,3-decadiene, 2,4-decadiene, 3,5-decadiene, or mixtures thereof. More preferably, the conjugated diene of formula (3) includes 1,3-butadiene, 1,3-pentadiene, or 1,3-hexadiene. Still more preferably, the conjugated diene of formula (3) includes 1,3-butadiene.

Generally, when the conjugated diene includes substantial amounts of 1,3-butadiene, the polymerized butadiene includes a mixture of 1,4- and 1,2-units. The preferred structures contain at least about 25% of the 1,2-units. More preferably, the structures contain from about 30% to about 90% of the 1,2-subunits. Most
5 preferably, the structures contain from about 45% to about 65% of the 1,2-units.

The polymers are prepared under anionic polymerization conditions. Following polymerization, the polymers of the invention are selectively hydrogenated to provide a controlled amount and extent of residual unsaturation. After the selective hydrogenation reaction, the hydrogenation catalyst is removed from the
10 polymer.

Accordingly, as a result of the invention, there are now provided personal care formulations with improved skin feel and film forming properties. The polymers and/or copolymers of the present invention enhance film forming by uniting materials which are not compatible under normal conditions by decreasing the
15 interfacial tension and allowing the formation of hydrogen bonding. The personal care formulations of the invention possess numerous advantages, including viscosity control, oxidative stability, compatibility, control of refractive index, glass transition temperature, melting point and solubility.

These and other advantages of the present invention will be appreciated from
20 the detailed description and examples which are set forth herein. The detailed description and examples enhance the understanding of the invention, but are not intended to limit the scope of the invention.

Therefore, the invention includes a personal care composition having film forming properties comprising a selectively hydrogenated polymer and/or copolymer
25 selected from the group consisting of isoprene, butadiene, styrene or mixtures thereof; water and at least one personal care agent.

The invention further includes a personal care composition having water resistant properties comprising a copolymer of a first conjugated diene and a second conjugated diene, wherein:

said first conjugated diene comprises at least one relatively more substituted conjugated diene having at least five carbon atoms and the formula:

(1)



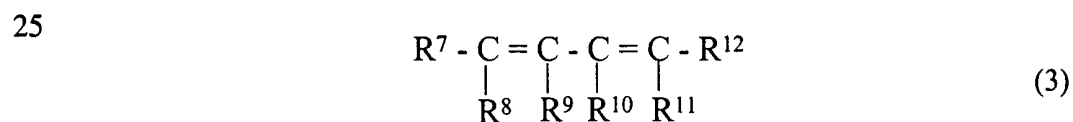
wherein R^1 - R^6 are each hydrogen or a hydrocarbyl group, provided that at least one of R^1 - R^6 is a hydrocarbyl group, provided that after polymerization, the unsaturation of the polymerized conjugated diene of formula (1) has the formula:

(2)



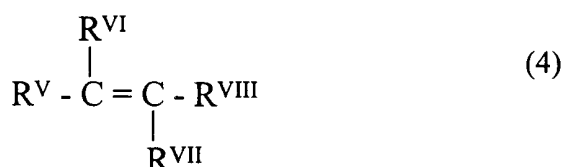
wherein R^I , R^{II} , R^{III} and R^{IV} are each hydrogen or a hydrocarbyl group, provided that either both R^I and R^{II} are hydrocarbyl groups or both R^{III} and R^{IV} are hydrocarbyl groups; and

said second conjugated diene comprises at least one relatively less substituted conjugated diene different from the first conjugated diene and having at least four carbon atoms and the formula:



wherein R^7 - R^{12} are each hydrogen or a hydrocarbyl group, provided that after polymerization, the unsaturation of the polymerized conjugated diene of formula (3) has the formula:

5



10 wherein R^V , R^{VI} , R^{VII} and R^{VIII} are each hydrogen or a hydrocarbyl group, provided that one of R^V or R^{VI} is hydrogen, one of R^{VII} or R^{VIII} is hydrogen, and at least one of R^V , R^{VI} , R^{VII} and R^{VIII} is a hydrocarbyl group.

and wherein said copolymer has been selectively hydrogenated to provide a selectively hydrogenated copolymer.

15

DETAILED DESCRIPTION OF THE INVENTION

This invention envisions all types of personal care or cosmetic compositions for topical treatment or application to human hair and skin.

20

The polymer component of the personal care formulation of the present invention provides an effective thickener, enhanced film forming and desired surface quality. Suitable polymer components include isoprene, butadiene and/or styrene homopolymers and copolymers. In one embodiment, the present invention provides personal care formulations comprising polymers including at least two different

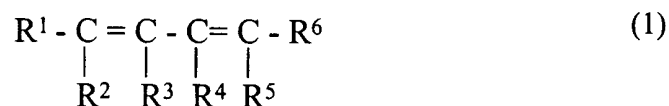
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conjugated dienes, wherein one of the dienes is more substituted in the 2, 3, and/or 4 carbon positions than the other diene. The more substituted diene produces vinylidene, tri-, or tetra-substituted double bonds after polymerization. Hydrogenation of the material is done selectively so as to saturate the lesser

substituted olefins, which primarily arise from the lesser substituted diene, while leaving a portion of the more substituted conjugated olefins.

In this embodiment, the more substituted conjugated diene will have at least five (5) carbon atoms and the following formula:

5



10 wherein R^1 - R^6 are each hydrogen (H) or a hydrocarbyl group, provided that at least one of R^1 - R^6 is a hydrocarbyl group. After polymerization, the unsaturation in the polymerized conjugated diene of formula (1) has the following formula:

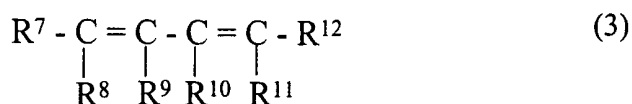
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wherein R^I , R^{II} , R^{III} and R^{IV} are each hydrogen or a hydrocarbyl group, provided that either both R^I and R^{II} are hydrocarbyl groups or both R^{III} and R^{IV} are hydrocarbyl groups. Examples of conjugated dienes of formula 1 include isoprene, 2,3-
20 dimethylbutadiene, 2-methyl-1,3-pentadiene, myrcene, and the like. Isoprene is highly preferred.

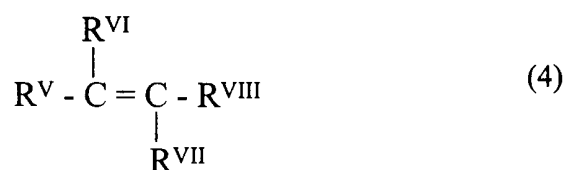
The lesser substituted conjugated diene in this embodiment differs from the other diene in that it has at least four (4) carbon atoms and the following formula:

25



wherein R^7 - R^{12} are each hydrogen or a hydrocarbyl group. After polymerization, the unsaturation in the polymerized conjugated diene of formula (3) has the following

5 formula:



10

wherein R^V , R^{VI} , R^{VII} and R^{VIII} are each hydrogen (H) or a hydrocarbyl group, provided that one of R^V or R^{VI} is hydrogen, one of R^{VII} or R^{VIII} is hydrogen, and at least one of R^V , R^{VI} , R^{VII} and R^{VIII} is a hydrocarbyl group. Examples of the

15 conjugated diene of formula (3) include 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, and the like. A highly preferred conjugated diene of formula 3 is 1,3-butadiene.

An exception to this scheme would be when a tetra-substituted diene, e.g., 2,3-dimethylbutadiene, is used for the more substituted component. When this occurs, a tri-substituted olefin, e.g. isoprene, may be used for the lesser substituted

20 component, such that one or both of R^V and R^{VI} are hydrogen and both R^{VII} and R^{VIII} are hydrocarbyl.

It will be apparent to those skilled in the art that in the original unsaturation of formula (2), R^I , R^{II} , R^{III} and R^{IV} may all be hydrocarbyl groups, whereas in the original unsaturation of formula (4) at least one of R^V , R^{VI} , R^{VII} and R^{VIII} must be a

25 hydrogen.

The hydrocarbyl group or groups in the formula (1) to (4) are the same or different and they are substituted or unsubstituted alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, or aralkyl groups, or any isomers thereof.

The copolymers of this embodiment are prepared by anionically polymerizing a diene of formula (1) at a level of from about 0.5% wt. to about 25% wt., and a diene of formula (3) at a level of from about 75% wt. to about 99.5% wt., in a hydrocarbon solvent using an alkylolithium catalyst. The two monomers can be polymerized in
5 block, tapered block, or random fashion. Since the polymerization is anionic, the molecular weight distribution of these copolymers is typically very narrow, generally ranging from about 1.01 to about 1.20, and the molecular weight is determined by the ratio of monomer to initiator and/or by the presence of coupling agents.

The monomers (1) and (3) may be polymerized either simultaneously or in
10 stepwise fashion depending on the desired position of the remaining unsaturation after hydrogenation. If random positioning of the unsaturation is desired, both monomers are reacted together to give a random copolymer. If it is desirable to have the unsaturation on only one end, then the monomers are reacted in stepwise fashion, the order being determined as desired, to provide a diblock copolymer. If
15 unsaturation is needed on both ends, then a conjugated diene of formula (1) is polymerized first, followed by a diene of formula (3). To the living anion, a coupling agent, e.g., phenyl benzoate or methyl benzoate, is then added to yield a desired triblock copolymer. Alternatively, a diene of formula (1) may be added to the living diblock to give the triblock. A fourth approach would allow the unsaturation to be
20 positioned in the center of the polymer chain. In this case, a diene of formula (3) is polymerized first, followed by a diene of formula (1). Then a triblock is formed by addition of a coupling agent or by addition of more diene of formula (3). In addition, combinations of the above approaches may be employed.

The invention can include polymers of differing microstructures. The
25 presence of polar modifier increases the activity of the catalyst and, therefore, increase the level of 1,2-microstructure over 1,4-microstructure in polybutadiene, for example. The percentage of vinyl obtained is directly proportional to the concentration of the modifier employed. Since the reaction temperature also plays a role in determining the microstructure of polybutadiene, the level of modifier must be

chosen taking into account the combined effects. Antkowiak et al., *Temperature and Concentration Effects on Polar-modified Alkyl Lithium Polymerizations and Copolymerizations*, Journal of Polymer Science: Part A-1, 10:1319-34 (1972), incorporated herein by reference have presented a way for quickly determining the proper conditions for preparation of any 1,2-microstructure content within a range of from about 10% to about 80%. Use of this method or any others to achieve the desired microstructure will be known to anyone who is skilled in the art.

The personal care formulations of the invention can include different polymer macrostructures. Polymers may be prepared and utilized having linear and/or nonlinear, e.g., star-branched, macrostructures to provide materials with varied rheological properties. For example, star polymers of equivalent molecular weight have lower bulk viscosity than linear polymers. The star-branched polymers can be prepared by addition of divinylbenzene or the like to the living polymer anion. Lower levels of branching can be obtained through the use of tri-functional or tetra-functional coupling agents, such as tetrachlorosilane.

In all embodiments of this invention, whenever a reference is made to the "original double bond" or the "original unsaturation" of the block or random polymer (or copolymer), it is understood to mean the double bond(s) in the polymer prior to the hydrogenation reaction. By contrast, the terms "residual double bond(s)" and "residual unsaturation", as used herein, refer to the unsaturated group(s), typically excluding aromatic unsaturation, present in the copolymer after the selective hydrogenation reaction.

The molecular structure of the original or residual double bonds can be determined in any conventional manner, as is known to those skilled in the art, e.g., by infrared (IR) or nuclear magnetic resonance (NMR) analysis. In addition, the total original or residual unsaturation of the polymer can be quantified in any conventional manner, e.g., by reference to the Iodine Number of the polymer.

In any polymers of any of the embodiments of this invention, the crystallinity of the polymer following the selective hydrogenation reaction is directly related to the

microstructure of the polymerized conjugated diene of formula (3). For example, if after the selective hydrogenation reaction the polymer must retain its elastomeric properties, then the polymer should contain not more than about 10% of polyethylene crystallinity. Control of polymeric crystallinity may be accomplished in various ways. For example, limiting crystallinity may be accomplished by introducing side branches into the polymerized conjugated dienes of formula (1) and/or (3), e.g., by controlling the microstructure of 1,3-butadiene if it is the predominant monomer in the diene of formula (3); by using a mixture of dienes of formula (3) containing less than predominant amounts of 1,3-butadiene; or by using a single diene of formula (3), other than 1,3-butadiene. More particularly, if the conjugated diene(s) of formula (3) is predominantly (at least 50% by mole) 1,3-butadiene, the side branches are introduced into the polymer by insuring that the polymerized diene of formula (3) contains a sufficient amount of the 1,2-units to prevent the selectively hydrogenated polymer from being excessively crystalline. Thus, if the conjugated diene of formula (3) is predominantly (at least 50% by mole, e.g., 100% by mole) 1,3-butadiene, the polymerized diene of formula (3), prior to the selective hydrogenation reaction, must contain not more than about 75% wt., preferably from about 10% wt. to about 70% wt., and most preferably from about 35% wt. to about 55% wt. of the 1,4-units, and at least about 25% wt., preferably from about 30% wt. to about 90% wt., and most preferably from about 45% wt. to about 65% wt. of the 1,2-units. If the polymerized diene(s) of formula (3) contains less than 50% by mole of 1,3-butadiene, e.g., 1,3-pentadiene is used as the only diene of formula (3), the microstructure of the polymerized diene of formula (3) prior to the selective hydrogenation reaction is not critical since, after hydrogenation, the resulting polymer will contain substantially no crystallinity. Alternatively, low melting solids (e.g. 25 to 35°C) may be prepared by controlling 1,2-units to 30 wt.% or less.

Homopolymers of a conjugated diene may be used to prepare polymers of the present invention in linear, branched or star branched form. The homopolymers may

be partially hydrogenated such that they possess an iodine number of 1-150, preferably 2-100. Mixtures of dienes of formula (1) or (3) may be used to prepare block or tapered block copolymers $(I)_x-(B)_y$ or any of the random copolymers or star-branched block, tapered block and random polymers of the invention. Similarly, mixtures of dienes and aryl-substituted olefins may also be used to prepare block, tapered block, random, or star-branched copolymers of this invention. Accordingly, whenever a reference is made herein to a diene of formula (1) or (3), or to an aryl-substituted olefin, it may encompass more than one diene of formula (1) or (3), respectively, and more than one aryl-substituted olefin.

10 The block copolymers of this invention comprise two or more alternating blocks, identified above. Linear block copolymers having two blocks and block copolymers having three or more blocks are contemplated herein.

 The block polymers useful according to the invention typically include at least one block which is substantially completely saturated, while also including at least one block containing controlled levels of unsaturation providing a hydrocarbon elastomer with selectively positioned unsaturation. For the copolymers prepared from two different conjugated dienes, it has been found that the two dienes in the copolymers hydrogenate at different rates, permitting selective control of the placement of residual unsaturation.

20 The many variations in composition, molecular weight, molecular weight distribution, relative block lengths, microstructure, branching, and T_g (glass transition temperature) attainable with the use of anionic techniques employed in the preparation of our polymers will be obvious to those skilled in the art.

 While not wishing to limit the molecular weight range of liquid elastomers prepared according to our invention, the minimum molecular weight for these liquid polymers is at least about 2,000, preferably above 3,000 to about 50,000, and most preferably about 5,000 to about 35,000. The star-branched block and random copolymers of this invention may have substantially higher molecular weights and still retain liquid properties.

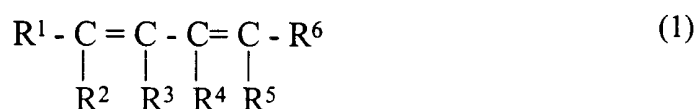
All numerical values of molecular weight given in this specification and the drawings are of number average molecular weight (M_n).

The invention will be described hereinafter in terms of the embodiments thereof summarized above. However, it will be apparent to those skilled in the art, that the invention is not limited to these particular embodiments, but, rather, it covers all the embodiments encompassed by the broadest scope of the description of the invention.

Copolymers From at Least Two Dissimilar Conjugated Dienes

In this embodiment of the invention, there are provided copolymers of two dissimilar conjugated dienes, preferably isoprene and 1,3-butadiene. The two monomers can be polymerized by anionic polymerization process in either a block, tapered block, or random fashion.

The copolymers of this embodiment include a first conjugated diene having at least five (5) carbon atoms and the following formula:

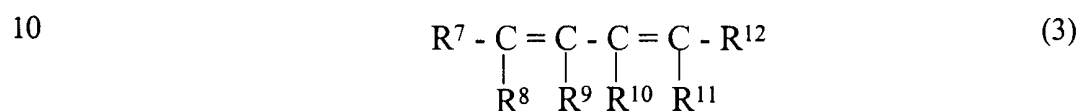


wherein R^1 - R^6 are each hydrogen or a hydrocarbyl group, provided that at least one of R^1 - R^6 is a hydrocarbyl group, and further provided that, when polymerized, the structure of the double bond in the polymerized conjugated diene of formula (1) has the following formula:



wherein R^I , R^{II} , R^{III} and R^{IV} are each hydrogen or a hydrocarbyl group, provided that either both R^I and R^{II} are hydrocarbyl groups or both R^{III} and R^{IV} are hydrocarbyl groups. In the double bond of the polymerized conjugated diene of formula (2), R^I , R^{II} , R^{III} and R^{IV} may all be hydrocarbyl groups.

The polymers of this embodiment also include a second conjugated diene, different from the first conjugated diene, having at least four (4) carbon atoms and the following formula:



wherein R^7 - R^{12} are each hydrogen or a hydrocarbyl group, provided that the structure of the double bond in the polymerized conjugated diene of formula (3) has the following formula:



wherein R^V , R^{VI} , R^{VII} and R^{VIII} are each hydrogen (H) or a hydrocarbyl group, provided that one of R^V or R^{VI} is hydrogen, one of R^{VII} or R^{VIII} is hydrogen, and at least one of R^V , R^{VI} , R^{VII} and R^{VIII} is a hydrocarbyl group.

The polymers of this embodiment include a first conjugated diene of formula (1) in an amount of at least about 0.5% wt., preferably at least about 1% wt., and

more preferably at least about 5% wt. The polymers of this embodiment include a first conjugated diene of formula (1) in an amount of at most about 30% wt., preferably at most about 25% wt., and more preferably at most about 20% wt. The second conjugated diene of formula (3) is an amount of at least about 70% wt., more
5 preferably at least about 75% wt., and more preferably at least about 80% wt. The second conjugated diene of formula (3) is in an amount of at most about 99.5% wt., preferably at most about 99% wt., and more preferably at most about 95% wt.

The polymers of this embodiment include block copolymers having at least two alternating blocks:

10 $(I)_x-(B)_y$ or $(B)_y-(I)_x$

In this case, the polymer includes at least one block (I). The block (I) is a block of at least one polymerized conjugated diene of formula (1) as described above.

These block copolymers also include at least one polymerized block (B). The block (B) is a block of at least one polymerized conjugated diene of formula (3) described
15 above.

In the block copolymers of this embodiment, x is at least 1, preferably from about 1 to about 600, and more preferably from about 1 to about 350. The above definition of x means that each of the (I) blocks is polymerized from at least 1, preferably about 1-600, and more preferably about 1-350, monomer units.

20 In the block copolymers of this embodiment, y is at least 25, preferably from about 30 to about 4,000, more preferably from about 30 to about 2,800. The above definition of y means that each of the (B) blocks is polymerized from at least 25, preferably about 30-4,000, and more preferably about 30-2,800, monomer units.

The block copolymer comprises about 0.5 to about 25%, preferably about 1 to
25 about 20% by wt. of the (I) blocks, and about 80 to about 99.5%, preferably about 80 to about 99% by wt. of the (B) blocks.

In any of the copolymers of this embodiment, the structures of the double bonds defined by formula (2) and (4) are necessary to produce copolymers which can

be selectively hydrogenated in the manner described herein, to produce the selectively hydrogenated block and random copolymers of this invention.

The hydrocarbyl group or groups in the formula (1) and (2) are the same or different and they are substituted or unsubstituted alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, or aralkyl groups, or any isomers thereof. Suitable hydrocarbyl groups are alkyls of 1-20 carbon atoms, alkenyls of 1-20 carbon atoms, cycloalkyls of 5-20 carbon atoms, aryls of 6-12 carbon atoms, alkaryl groups of 7-20 carbon atoms or aralkyls of 7-20 carbon atoms. Examples of suitable alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, methyl-decyl or dimethyl-decyl. Examples of suitable alkenyl groups are ethenyl, propenyl, butenyl, pentenyl or hexenyl. Examples of suitable cycloalkyl groups are cyclohexyl or methylcyclohexyl. Examples of suitable cycloalkenyl groups are 1-, 2-, or 3-cyclohexenyl or 4-methyl-2-cyclohexenyl. Examples of suitable aryl groups are phenyl or diphenyl. Examples of suitable alkaryl groups are 4-methyl-phenyl (p-tolyl) or p-ethyl-phenyl. Examples of suitable aralkyl groups are benzyl or phenethyl. Suitable conjugated dienes of formula (1) used to polymerize the (I) block are isoprene, 2,3-dimethyl-butadiene, 2-methyl-1,3-pentadiene, myrcene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, 2-phenyl-1,3-pentadiene, 3-phenyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-hexyl-1,3-butadiene, 3-methyl-1,3-hexadiene, 2-benzyl-1,3-butadiene, 2-p-tolyl-1,3-butadiene, or mixtures thereof, preferably isoprene, myrcene, 2,3-dimethyl-butadiene, or 2-methyl-1,3-pentadiene, and most preferably isoprene.

The hydrocarbyl group or groups in the formula (3) may or may not be the same as those in formula (4). These hydrocarbyl groups are the same as those described above in conjunction with the discussion of the hydrocarbyl groups of formula (1) and (2). Suitable monomers for the (B) block are 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, 1,3-hexadiene, 1,3-heptadiene, 2,4-heptadiene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3-nonadiene, 2,4-nonadiene, 3,5-nonadiene, 1,3-decadiene, 2,4-decadiene, 3,5-decadiene, or mixtures thereof,

preferably 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, or 1,3-hexadiene, and most preferably it is 1,3-butadiene. It is generally preferred that each of the (B) blocks is polymerized from a single monomer.

The scope of this embodiment, and of any other embodiments of the invention wherein the block (B) is used, also encompasses polymers wherein the block (B) may 5 comprise copolymers of one or more conjugated diene of formula (3) and controlled amounts (about 0.3 to about 50 mole %) of an aryl-substituted olefin, e.g., styrene or other suitable monomers (such as alkylated styrene, vinyl naphthalene, or alkylated vinyl naphthalene) incorporated for control of glass transition temperature (T_g), 10 density, solubility parameters and refractive index. Similarly, the scope of this embodiment also encompasses polymers wherein the block (B) may be comprised of copolymers of one or more conjugated diene of formula (3) and any other anionically polymerizable monomer capable of polymerizing with the conjugated diene of formula (3). Similar considerations also apply in the case of the (I) block(s), which 15 can include similar styrene/diene copolymers.

The copolymer is polymerized by anionic polymerization, discussed in detail below. As will be apparent to those skilled in the art, the block copolymer of this embodiment contains at least two alternating blocks, (I)-(B) or (B)-(I), referred to herein as diblocks. The block copolymer of this embodiment may contain three 20 alternating blocks, e.g., (I)-(B)-(I), referred to herein as triblocks or triblock units, but it may contain an unlimited number of blocks. The functionalization of any of these copolymers is conducted in a conventional manner and is described below.

After the (I)-(B) copolymer is polymerized, it is subjected to a selective hydrogenation reaction during which the polymerized conjugated dienes of formula 25 (1) and (3) of the copolymer are selectively hydrogenated to the desired extent.

Generally, for a copolymer wherein the conjugated dienes of formula (1) and (3) are polymerized to provide unsaturation of formula (2) and (4), respectively, as discussed above, the Iodine Number for the unsaturation of formula (2) after the selective hydrogenation reaction is from about 20% to about 100%, preferably from

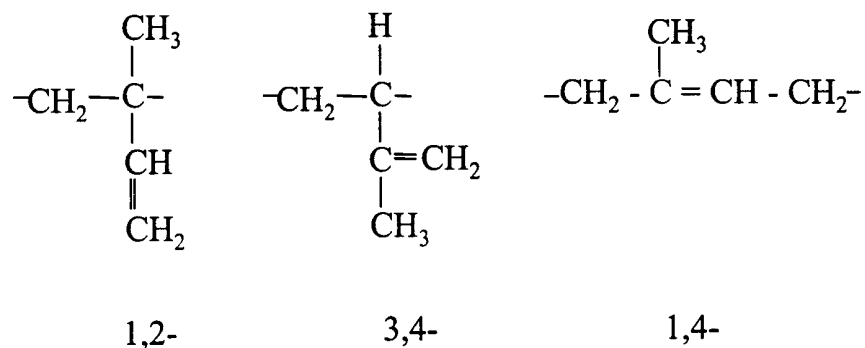
about 50% to about 100%, and most preferably about 100%, of the Iodine Number prior to the selective hydrogenation reaction; and for the unsaturation of formula (4) it is from about 0% to about 10%, preferably from about 0% to about 0.5%, and most preferably from about 0% to about 0.2%, of the Iodine Number prior to the selective

5 hydrogenation reaction. The Iodine Number, as is known to those skilled in the art, is defined as the theoretical number of grams of iodine which will add to the unsaturation in 100 grams of olefin and is a quantitative measure of unsaturation.

In this embodiment of the invention, although the microstructure of the (I) blocks is not critical and may consist of 1,2-, 3,4- and/or 1,4-units, schematically

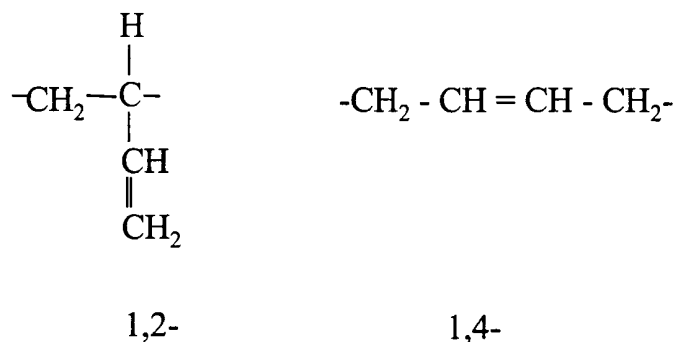
10 represented below for the polyisoprene blocks, when a polar compound is used during the polymerization of the (I) block, the (I) blocks comprise primarily (at least about 50% wt.) 3,4-units, the rest being primarily (less than about 50% wt.) 1,4-units; when the polar compound is not used during the polymerization of the (I) block, the (I) blocks comprise primarily (about 80% wt.) 1,4-units, the rest being primarily 1,2- and

15 3,4- units.



The microstructure of the (B) blocks, when the predominant monomer used to polymerize the (B) blocks is 1,3-butadiene, should be a mixture of 1,4- and 1,2- units

20 schematically shown below for the polybutadiene blocks:



since the hydrogenation of the predominantly 1,4-microstructure produces a crystalline polyethylene segment. The microstructure of the (I) and (B) blocks (as well as of the polymerized conjugated dienes of formula (1) or (3) in any polymers of this invention) is controlled in a conventional manner, e.g., by controlling the amount and nature of the polar compounds used during the polymerization reaction, and the reaction temperature. In one particularly preferred embodiment, the (B) block contains about 50% of the 1,2- and about 50% of the 1,4- microstructure. If the (B) block is poly-1,3-butadiene, the hydrogenation of the (B) segment containing from about 50% to about 60% of the 1,2-microstructure content produces an elastomeric center block which is substantially an ethylene-butene-1 copolymer having substantially no crystallinity. If the (B) block is polymerized from 1,3-pentadiene, the microstructure is not critical.

The terms "1,2-", "1,4-", and "3,4-microstructure" or "units" as used in this application refer to the products of polymerization obtained by the 1,2-, 1,4- and 3,4-, respectively, mode of addition of monomer units.

We surprisingly discovered that the polymerized conjugated dienes of formula (3), e.g., the dienes employed in (B) blocks, of the polymers of this invention are selectively hydrogenated in our hydrogenation process much faster than the polymerized conjugated dienes of formula (1), e.g., the dienes used in the (I) blocks. This is not evident from the teachings of Falk, discussed above, because Falk teaches that double bonds of the di-substituted 1,4-polybutadiene units are hydrogenated selectively in the presence of double bonds of the tri-substituted 1,4-polyisoprene units (which hydrogenate very slowly). We surprisingly discovered that the di-

substituted double bonds of the 1,4-polybutadiene units are hydrogenated along with the monosubstituted double bonds of the 1,2-polybutadiene units, while the di-substituted double bonds of the 3,4-polyisoprene units are hydrogenated at a much slower rate than the aforementioned polybutadienes. Thus, in view of Falk's

5 disclosure it is surprising that the di-substituted double bonds of the 1,4-polybutadiene units are hydrogenated selectively in the presence of the di-substituted double bonds of the 3,4-polyisoprene units. This is also surprising in view of the teachings of Hoxmeier, Published European Patent Application, Publication No. 0 315 280, who discloses that the di-substituted double bonds of the 1,4-polybutadiene

10 units, monosubstituted double bonds of the 1,2-polybutadiene units and di-substituted double bonds of the 3,4-polyisoprene units are hydrogenated simultaneously at substantially the same rates. For example, for the block copolymers of this invention, wherein the (I) block is polyisoprene and the (B) block is polybutadiene, Fourier Transform Infrared (FTIR) analysis of selectively hydrogenated block copolymers of

15 the invention, such as I-B-I triblock polymers, indicates that the hydrogenation of the double bonds of the 1,2-polybutadiene units proceeds most rapidly, followed by the hydrogenation of the double bonds of the 1,4-polybutadiene units. Infrared absorptions caused by these groups disappear prior to appreciable hydrogenation of the polyisoprene units.

20 Accordingly, by controlling the amount and placement of 1,2- versus 1,4-microstructure, as well as the amount and placement of polyisoprene units, it is now possible to control the amount and placement of unsaturation remaining in the polymers after hydrogenation.

After the block copolymer is prepared, it is subjected to a selective

25 hydrogenation reaction to hydrogenate primarily the (B) block(s). The selective hydrogenation reaction and the catalyst are described in detail below. After the hydrogenation reaction is completed, the selective hydrogenation catalyst is removed from the block copolymer, and the polymer is isolated by conventional procedures, e.g., alcohol flocculation, steam stripping of solvent, or non-aqueous solvent

evaporation. An antioxidant, e.g., vitamin E, is normally added to the polymer solution prior to polymer isolation.

Random Copolymers

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Random copolymers of this invention have controlled amounts of unsaturation incorporated randomly in an otherwise saturated backbone. In contrast to EPDM, the level of unsaturation can be easily controlled, e.g., to produce polymers having Iodine Number of from about 5 to about 100, to provide a wide variety of polymer properties.

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In one embodiment, the random copolymers are polymerized from the same monomers used to polymerize the block copolymers $(I)_x-(B)_y$, described elsewhere herein. In particular, the random copolymers may be made by polymerizing at least one conjugated diene of formula (1) with at least one conjugated diene of formula (3), both defined above. This random copolymer contains from about 1.0% to about 40%, preferably from about 1.0% to about 20%, by mole of the polymerized conjugated diene of formula (1) and from about 60% to about 99%, preferably from about 80% to about 99% by mole of the polymerized conjugated diene of formula (3). Suitable conjugated dienes of formula (1) are exemplified above. The most preferred conjugated diene of formula (1) for the copolymerization of these random copolymers is isoprene. Suitable conjugated dienes of formula (3) are also exemplified above. The most preferred conjugated diene of formula (3) is 1,3-butadiene for the polymerization of the random copolymer of this embodiment. Thus, most preferably, in this embodiment, the random copolymer is polymerized from isoprene and 1,3-butadiene, and it contains from about 1% wt. to about 20% wt. of the isoprene units and from about 80% wt. to about 99% wt. of the butadiene units. The isoprene units have primarily (i.e., from about 50% wt. to about 90% wt.) the 3,4-microstructure.

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The random copolymers are subjected to the selective hydrogenation reaction discussed above for the block copolymers.

Star-Branched Polymers

The invention is also directed to star-branched block and random polymers.

- 5 The star-branched block polymers are made from any combination of blocks (I) and (B), defined above.

The star-branched (I)-(B) block polymers comprise from about 0.5% wt. to about 25% wt., preferably from about 1% wt. to about 20% wt., of the (I) blocks, and from about 75% wt. to about 99.5% wt., preferably from about 80% wt. to about 99%
10 wt., of the (B) blocks.

The star-branched block polymers are selectively hydrogenated in the selective hydrogenation process of this invention to such an extent that blocks (B) contain substantially none of the original unsaturation, while each of the blocks (I) respectively, retains a sufficient amount of the original unsaturation of the conjugated
15 dienes present in these blocks to functionalize the star-branched block polymers. Thus, for the I-(B) star-branched block polymer, after the selective hydrogenation reaction, the Iodine Number for the (I) blocks is from about 10% to about 100%, preferably from about 25% to about 100%, more preferably from about 50% to about 100%, and most preferably about 100%, of the Iodine Number prior to the selective
20 hydrogenation reaction; and for the (B) blocks it is from about 0% to about 10%, preferably from about 0% to about 0.5%, of the Iodine Number prior to the selective hydrogenation reaction.

The star-branched random polymers are made from any combination of at least one diene of formula (1) and at least one diene of formula (3), different from the
25 diene of formula (1), or from any combination of at least one aryl-substituted olefin and at least one diene of formula (1) or (3), all of which are the same as those discussed above. The star-branched random polymers of the dienes of formula (1) and (3), which must be different from each other, comprise from about 0.5% wt. to about 25% wt., preferably from about 1% wt. to about 20% wt., of the diene of

formula (1), and from about 75% wt. to about 99.5% wt., preferably from about 80% wt. to about 99% wt., of the diene of formula (3). The star-branched random polymers of the aryl-substituted olefin and the diene of formula (1) or (3) comprise from about 0.5% wt. to about 50% wt., preferably from about 1% wt. to about 25% wt., of the aryl-substituted olefin, and from about 50% wt. to about 99.5% wt., preferably from about 75% wt. to about 99% wt., of the diene of formula (1) or (3).

The star-branched random diene polymers are also subjected to the selective hydrogenation reaction discussed above for the block copolymers.

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Polymerization Reaction

The polymers of this invention are polymerized by any known polymerization processes, preferably by an anionic polymerization process. Anionic polymerization is well known in the art and it is utilized in the production of a variety of commercial polymers. An excellent comprehensive review of the anionic polymerization processes appears in the text Advances in Polymer Science 56, *Anionic Polymerization*, pp. 1-90, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo 1984 in a monograph entitled Anionic Polymerization of Non-polar Monomers Involving Lithium, by R.N. Young, R.P. Quirk and L.J. Fetters, incorporated herein by reference. The anionic polymerization process is conducted in the presence of a suitable anionic catalyst (also known as an initiator), such as n-butyl-lithium, sec-butyl-lithium, t-butyl-lithium, sodium naphthalide or, cumyl potassium. The amount of the catalyst and the amount of the monomer in the polymerization reaction dictate the molecular weight of the polymer. The polymerization reaction is conducted in solution using an inert solvent as the polymerization medium, e.g., aliphatic hydrocarbons, such as hexane, cyclohexane, or heptane, or aromatic solvents, such as benzene or toluene. In certain instances, inert polar solvents, such as tetrahydrofuran, can be used alone as a solvent, or in a mixture with a hydrocarbon solvent.

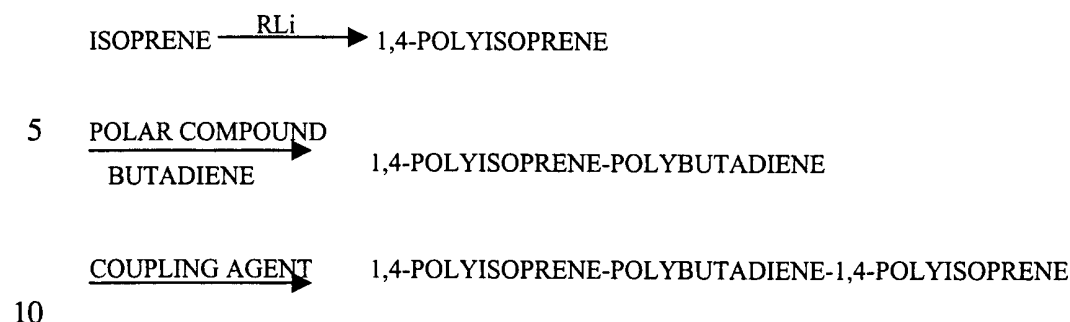
The polymerization process will be exemplified below for the polymerization of one of the embodiments of the invention, e.g., a triblock of polyisoprene-polybutadiene-polyisoprene. However, it will be apparent to those skilled in the art that the same process principles can be used for the polymerization of all polymers of the invention.

The process, when using a lithium-based catalyst, comprises forming a solution of the isoprene monomer in an inert hydrocarbon solvent, such as cyclohexane, modified by the presence therein of one or more polar compounds selected from the group consisting of ethers, thioethers, and tertiary amines, e.g., tetrahydrofuran. The polar compounds are necessary to control the microstructure of the butadiene center block, i.e., the content of the 1,2-structure thereof. The higher the content of the polar compounds, the higher will be the content of the 1,2-structure in these blocks. Since the presence of the polar compound is not essential in the formation of the first polymer block with many initiators unless a high 3,4-structure content of the first block is desired, it is not necessary to introduce the polar compound at this stage, since it may be introduced just prior to or together with the addition of the butadiene in the second polymerization stage. Examples of polar compounds which may be used are dimethyl ether, diethyl ether, ethyl methyl ether, ethyl propyl ether, dioxane, diphenyl ether, dipropyl ether, tripropyl amine, tributyl amine, trimethyl amine, triethyl amine, and N-N'-N'-N'-tetramethyl ethylene diamine. Mixtures of the polar compounds may also be used. The amount of the polar compound depends on the type of the polar compound and the polymerization conditions as will be apparent to those skilled in the art. The effect of polar compounds on the polybutadiene microstructure is detailed in Antkowiak et al. The polar compounds also accelerate the rate of polymerization. If monomers other than 1,3-butadiene, e.g., pentadiene, are used to polymerize the central blocks (B), polar compounds are not necessary to control the microstructure because such monomers will inherently produce polymers which do not possess crystallinity after hydrogenation.

When the alkyl lithium-based initiator, a polar compound and an isoprene monomer are combined in an inert solvent, polymerization of the isoprene proceeds to produce the first terminal block whose molecular weight is determined by the ratio of the isoprene to the initiator. The living polyisoprenyl anion formed in this first
5 step is utilized as the catalyst for further polymerization. At this time, butadiene monomer is introduced into the system and block polymerization of the second block proceeds, the presence of the polar compound now influencing the desired degree of branching (1,2-structure) in the polybutadiene block. The resulting product is a living diblock polymer having a terminal anion and a lithium counterion. The living
10 diblock polymer serves as a catalyst for the growth of the final isoprene block, formed when isoprene monomer is again added to the reaction vessel to produce the final polymer block, resulting in the formation of the I-B-I triblock. Upon completion of polymerization, the living anion, now present at the terminus of the triblock, is destroyed by the addition of a proton donor, such as methyl alcohol or acetic acid.
15 The polymerization reaction is usually conducted at a temperature of between about 0°C and about 100°C, although higher temperatures can be used. Control of a chosen reaction temperature is desirable since it can influence the effectiveness of the polar compound additive in controlling the polymer microstructure. The reaction temperature can be, for example, from about 50°C to about 80°C. The reaction
20 pressure is not critical and varies from about atmospheric to about 100 psig.

If the polar compounds are utilized prior to the polymerization of the first (I) segment, (I) blocks with high 3,4-unit content are formed. If polar compounds are added after the initial (I) segment is prepared, the first (I) segment will possess a high percentage of 1,4-microstructure (which is tri-substituted), and the second (I) segment
25 will have a high percentage of 3,4-microstructure.

The production of triblock polymers having a high 1,4-unit content on both of the terminal (I) blocks is also possible by the use of coupling techniques illustrated below for a polyisoprene-polybutadiene-polyisoprene block copolymer:



The substitution of myrcene for the isoprene during the polymerization of the (I) blocks insures the incorporation of a high proportion of tri-substituted double bonds, even in the presence of polar compounds since myrcene contains a pendant tri-

15 substituted double bond which is not involved in the polymerization process. In a coupling process, similar to that described above, block polymers containing polyisoprene end blocks (or any other polymerized monomer suitable for use in the (I) block) having a high 3,4-microstructure content can be obtained by adding the polar compound prior to the isoprene (or another monomer) polymerization.

20 The use of the coupling technique for the production of triblock polymers reduces the reaction time necessary for the completion of polymerization, as compared to sequential addition of isoprene, followed by butadiene, followed by isoprene. Such coupling techniques are well known and utilize coupling agents such as esters, CO₂, iodine, dihaloalkanes, silicon tetrachloride, divinyl benzene, alkyl

25 trichlorosilanes and dialkyl dichlorosilanes. The use of tri- or tetra-functional coupling agents, such as alkyl trichlorosilanes or silicon tetrachloride, permits the formation of macromolecules having 1- or 2- main chain branches, respectively. The addition of divinyl benzene as a coupling agent has been documented to produce molecules having up to 20 or more separately joined segments.

30 The use of some of the coupling agents provides a convenient means of producing star-branched block and random polymers. The star-branched block

The use of some of the coupling agents provides a convenient means of producing star-branched block and random polymers. The star-branched block polymers are made from any combination of blocks (I) and (B), defined above. The star-branched random polymers are made from any combination of at least one diene of formula (1) and at least one diene of formula (3), different from the diene of formula (1), or from at least one aryl-substituted olefin, at least one diene of formula (1) and at least one diene of formula (3), different from the diene of formula (1). The molecular weight of the star-branched block and random copolymers will depend on the number of branches in each such copolymer, as will be apparent to those skilled in the art. Suitable coupling agents and reactions are disclosed in the following references which are incorporated herein by reference: U.S. Patent Nos. 3,949,020; 3,594,452; 3,598,887; 3,465,065; 3,078,254; 3,766,301; 3,632,682; 3,668,279; and Great Britain patent Nos. 1,014,999; 1,074,276; 1,121,978.

Hydrogenation

Following polymerization, the polymers may be selectively hydrogenated, partially hydrogenated or completely hydrogenated. Selective hydrogenation of the polymer may be accomplished using techniques similar to those known in the art. A preferred method and catalyst are described in U.S. Patent No. 5,187,236, the disclosure of which is incorporated herein by reference. The procedure and catalyst are described in greater detail below. In general, however, the previously described polymers can be contacted with hydrogen and a hydrogenation catalyst synthesized from a transition metal compound, typically nickel or cobalt, and an organometallic reducing agent, e.g., triethylaluminum. The hydrogenation proceeds at temperatures typically not in excess of about 40°C and at pressures of from about 30 psi to about 200 psi. Generally, the polymers are hydrogenated such that substantially all of the unsaturation in formula (4) is removed, while much of that from formula (2) is retained.

The selective hydrogenation reaction will also be described below using a triblock of polyisoprene-polybutadiene-polyisoprene as an example. However, it will be apparent to those skilled in the art that any polymers of this invention can be selectively hydrogenated in the same manner.

5 In Example II below, the block copolymer is selectively hydrogenated to saturate the middle (polybutadiene) block. The method of selectively hydrogenating the polybutadiene block is similar to that of Falk, *Coordination Catalysts for the Selective Hydrogenation of Polymeric Unsaturation*, Journal of Polymer Science: Part A-1, 9:2617-23 (1971), but it is conducted with a novel hydrogenation catalyst
10 and process used herein. Any other known selective hydrogenation methods may also be used, as will be apparent to those skilled in the art, but it is preferred to use the method described herein. In summary, the selective hydrogenation method preferably used herein comprises contacting the previously-prepared block copolymer with hydrogen in the presence of the novel catalyst composition.

15 The novel hydrogenation catalyst composition and hydrogenation process are described in detail in previously cited Application Serial No. 07/466,136. The hydrogenation catalyst composition is synthesized from at least one transition metal compound and an organometallic reducing agent. Suitable transition metal
20 compounds are compounds of metals of Group IVb, Vb, VIb or VIII, preferably IVb or VIII of the Periodic Table of the Elements, published in Lange's Handbook of Chemistry, 13th Ed., McGraw-Hill Book Company, New York (1985) (John A. Dean, ed.). Non-limiting examples of such compounds are metal halides, e.g., titanium tetrachloride, vanadium tetrachloride; vanadium oxytrichloride, titanium and
25 vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl radical of 1 to about 20 carbon atoms, preferably 1 to about 6 carbon atoms. Preferred transition metal compounds are metal carboxylates or alkoxides of Group IVb or VIII of the Periodic Table of the Elements, such as nickel (II) 2-ethylhexanoate, titanium isopropoxide, cobalt (II) octoate, nickel (II) phenoxide and ferric acetylacetonate.

The organometallic reducing agent is any one or a combination of any of the materials commonly employed to activate Ziegler-Natta olefin polymerization catalyst components containing at least one compound of the elements of Groups Ia, IIa, IIb, IIIa, or IVa of the Periodic Table of the Elements. Examples of such

5 reducing agents are metal alkyls, metal hydrides, alkyl metal hydrides, alkyl metal halides, and alkyl metal alkoxides, such as alkyllithium compounds, dialkylzinc compounds, trialkylboron compounds, trialkylaluminum compounds, alkylaluminum halides and hydrides, and tetraalkylgermanium compounds. Mixtures of the reducing agents may also be employed. Specific examples of useful reducing agents include n-

10 butyllithium, diethylzinc, di-n-propylzinc, triethylboron, diethylaluminummethoxide, triethylaluminum, trimethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, ethylaluminum dichloride, dibromide, and dihydride, isobutyl aluminum dichloride, dibromide, and dihydride, diethylaluminum chloride, bromide, and hydride, di-n-propylaluminum chloride, bromide, and hydride, diisobutylaluminum chloride,

15 bromide and hydride, tetramethylgermanium, and tetraethylgermanium.

Organometallic reducing agents which are preferred are Group IIIa metal alkyls and dialkyl metal halides having 1 to about 20 carbon atoms per alkyl radical. More preferably, the reducing agent is a trialkylaluminum compound having 1 to about 6 carbon atoms per alkyl radical. Other reducing agents which can be used herein are

20 disclosed in Stevens et al., U.S. Patent No. 3,787,384, column 4, line 45 to column 5, line 12 and in Strobel et al., U.S. Patent No. 4,148,754, column 4, line 56 to column 5, line 59, the entire contents of both of which are incorporated herein by reference. Particularly preferred reducing agents are metal alkyl or hydride derivatives of a metal selected from Groups Ia, IIa and IIIa of the Periodic Table of the Elements,

25 such as n-butyl lithium, sec-butyl lithium, n-hexyl lithium, phenyl-lithium, triethylaluminum, tri-isobutylaluminum, trimethyl-aluminum, diethylaluminum hydride and dibutylmagnesium.

The molar ratio of the metal derived from the reducing agent to the metal derived from the transition metal compound will vary for the selected combinations

of the reducing agent and the transition metal compound, but in general it is about 1:1 to about 12:1, preferably about 1.5:1 to about 8:1, more preferably about 2:1 to about 7:1, and most preferably about 2.5:1 to about 6:1. It will be apparent to those skilled in the art that the optimal ratios will vary depending upon the transition metal and the organometallic agent used, e.g., for the trialkylaluminum/nickel(II) systems, the preferred aluminum: nickel molar ratio is about 2.5:1 to about 4:1, for the trialkylaluminum/cobalt(II) systems, the preferred aluminum: cobalt molar ratio is about 3:1 to about 4:1, and for the trialkylaluminum/titanium(IV) alkoxides systems, the preferred aluminum: titanium molar ratio is about 3:1 to about 6:1.

The mode of addition and the ratio of the reducing agent to the transition metal compound are important in the production of the novel hydrogenation catalyst having superior selectivity, efficiency and stability, as compared to prior art catalytic systems. During the synthesis of the catalysts it is preferred to maintain the molar ratio of the reactants used to synthesize the catalyst substantially constant. This can be done either by the addition of the reducing agent, as rapidly as possible, to a solution of the transition metal compound, or by a substantially simultaneous addition of the separate streams of the reducing agent and the transition metal compound to a catalyst synthesis vessel in such a manner that the selected molar ratios of the metal of the reducing agent to the metal of the transition metal compound are maintained substantially constant throughout substantially the entire time of addition of the two compounds. The time required for the addition must be such that excessive pressure and heat build-up are avoided, i.e., the temperature should not exceed about 80 °C and the pressure should not exceed the safe pressure limit of the catalyst synthesis vessel.

In a preferred embodiment, the reducing agent and the transition metal compound are added substantially simultaneously to the catalyst synthesis vessel in such a manner that the selected molar ratio of the reducing agent to the transition metal compound is maintained substantially constant during substantially the entire time of the addition of the two compounds. This preferred embodiment permits the

control of the exothermic reaction so that the heat build-up is not excessive, and the rate of gas production during the catalyst synthesis is also non excessive -- accordingly, the gas build-up is relatively slow. In this embodiment, carried out with or without a solvent diluent, the rate of addition of the catalyst components is

5 adjusted to maintain the synthesis reaction temperature at or below about 80°C, which promotes the formation of the selective hydrogenation catalyst. Furthermore, the selected molar ratios of the metal of the reducing agent to the metal of the transition metal compound are maintained substantially constant throughout the entire duration of the catalyst preparation when the simultaneous mixing technique of this
10 embodiment is employed.

In another embodiment, the catalyst is formed by the addition of the reducing agent to the transition metal compound. In this embodiment, the timing and the order of addition of the two reactants is important to obtain the hydrogenation catalyst having superior selectivity, efficiency and stability. Thus, in this embodiment, it is
15 important to add the reducing agent to the transition metal compound in that order in as short a time period as practically possible. In this embodiment, the time allotted for the addition of the reducing agent to the transition metal compound is critical for the production of the novel catalyst. The term "as short a time period as practically possible" means that the time of addition is as rapid as possible, such that the reaction
20 temperature is not higher than about 80°C and the reaction pressure does not exceed the safe pressure limit of the catalyst synthesis vessel. As will be apparent to those skilled in the art, that time will vary for each synthesis and will depend on such factors as the types of the reducing agents, the transition metal compounds and the solvents used in the synthesis, as well as the relative amounts thereof, and the type of
25 the catalyst synthesis vessel used. For purposes of illustration, a solution of about 15 mL of triethylaluminum in hexane should be added to a solution of nickel(II) octoate in mineral spirits in about 10-30 seconds. Generally, the addition of the reducing agent to the transition metal compound should be carried out in about 5 seconds (sec) to about 5 minutes (min), depending on the quantities of the reagents used. If the

time period during which the reducing agent is added to the transition metal compound is prolonged, e.g., more than 15 minutes, the synthesized catalyst is less selective, less stable, and may be heterogeneous.

In the embodiment wherein the reducing agent is added as rapidly as possible to the transition metal compound, it is also important to add the reducing agent to the transition metal compound in the aforementioned sequence to obtain the novel catalyst. The reversal of the addition sequence, i.e., the addition of the transition metal compound to the reducing agent, or the respective solutions thereof, is detrimental to the stability, selectivity, activity, and homogeneity of the catalyst and is, therefore, undesirable.

In all embodiments of the hydrogenation catalyst synthesis, it is preferred to use solutions of the reducing agent and the transition metal compound in suitable solvents, such as hydrocarbon solvents, e.g., cyclohexane, hexane, pentane, heptane, benzene, toluene, or mineral oils. The solvents used to prepare the solutions of the reducing agent and of the transition metal compound may be the same or different, but if they are different, they must be compatible with each other so that the solutions of the reducing agent and the transition metal compound are fully soluble in each other.

The hydrogenation process comprises contacting the unsaturated polymer to be hydrogenated with an amount of the catalyst solution containing at least about 0.1 and preferably at least about 0.2 mole percent of the transition metal based on moles of the polymer unsaturation. The amount of the catalyst solution containing at most about 0.5 and preferably at most 0.3 mole percent of the transition metal based on moles of the polymer unsaturation. The hydrogen partial pressure is generally from about 5 psig to about several hundred psig, but preferably it is from about 10 psig to about 100 psig. The temperature of the hydrogenation reaction mixture is generally at least about 0 °C, preferably at least about 35°C, and more preferably at least about 30 °C. The temperature of the hydrogenation reaction mixture is generally at most about 150 °C, preferably at most about 80°C, and more preferably at most about 60°C,

since higher temperatures may lead to catalyst deactivation. The length of the hydrogenation reaction may be as short as 30 minutes and, as will be apparent to those skilled in the art, depends to a great extent on the actual reaction conditions employed. The hydrogenation process may be monitored by any conventional means, 5 e.g., infra-red spectroscopy, hydrogen flow rate, total hydrogen consumption, or any combination thereof.

Upon completion of the hydrogenation process, unreacted hydrogen is either vented or consumed by the introduction of the appropriate amount of an unsaturated material, such as 1-hexene, which is converted to an inert hydrocarbon, e.g., hexane. 10 Subsequently, the catalyst is removed from the resulting polymer solution by any suitable means, selected depending on the particular process and polymer. For a low molecular weight material, for example, catalyst residue removal may consist of a treatment of the solution with an oxidant, such as air, and subsequent treatment with ammonia and optionally methanol in amounts equal to the molar amount of the 15 metals (i.e., the sum of the transition metal and the metal of the reducing agent) present in the hydrogenation catalyst to yield the catalyst residues as a filterable precipitate, which is filtered off. The solvent may then be removed by any conventional methods, such as vacuum stripping, to yield the product polymer as a clear, colorless fluid.

20 Alternatively, and in a preferred embodiment, upon completion of the hydrogenation reaction, the mixture is treated with ammonia in the molar amount about equal to that of the metals (i.e., the sum of the transition metal and the metal of the reducing agent) and aqueous hydrogen peroxide, in the molar amount equal to about one half to about one, preferably one half, of the amount of the metals. Other 25 levels of the ammonia and peroxide are also operative, but those specified above are particularly preferred. In this method, a precipitate forms, which may be filtered off as described above.

In yet another alternative method, the catalyst may be removed by extraction with an aqueous mineral acid, such as sulfuric, phosphoric, or hydrochloric acid,

followed by washing with distilled water. A small amount of a material commonly used as an aid in removing transition metal-based catalysts, such as a commercially available high molecular weight diamine, e.g., Jeffamine D-2000 from Huntsman, may be added to aid in phase separation and catalyst removal during the extractions.

5 The resultant polymer solution is then dried over a drying agent, such as magnesium sulfate, separated from the drying agent and the solvent is then separated by any conventional methods, such as vacuum stripping, to yield a polymer as a clear fluid. Other methods of polymer isolation, such as steam or alcohol flocculation, may be employed depending upon the hydrogenated polymer properties.

10 After hydrogenation and purification is complete, the polymer can be incorporated into a variety of skin and hair care product formulations.

Product Formulations

15 The present invention is useful for all types of personal care or cosmetic compositions for topical treatment of or application to human hair or skin including but not limited to hand, facial and scalp cleansers, shampoos, antiperspirants, deodorants, skin conditioners, night creams, moisturizers, refreshers, softeners, wrinkle, itch blemish and acne reducers and inhibitors, sunscreens, insect repellants,
20 topical analgesics, antiseptics and wound protectants, shave and aftershave preparations, hair conditioners, colorants, rinses, and fixatives, foam baths, bodywash and the like.

Personal care products for the care of human skin and hair contain a base incorporating the special reagent chosen for the specific use being considered. In
25 these bases, for example, different active materials and perfume oils can be incorporated, often with water. The bases themselves should not only be carriers of active materials but should also provide additional benefits if possible. For example, the base materials may help protect from external damage and exert a positive influence on the moisture content of the skin or hair. Accordingly, different base

materials have been developed for use in personal care applications aimed at the care of human skin and hair.

Various personal care agents may be incorporated in the personal care compositions of the present invention including but not limited to whitening agents, pigments, dyes, fragrances, pH controllers, foam improvers and stabilizers, opacifying agents, preservatives, silicones, chlorophyll compounds, humectant, conditioners, anionic surfactants, superfatting agents, antiseptics, solvents, UV absorbers, oxidizing and reducing agents, antidandruff and/or ammoniated material such as urea, diammonium phosphate and mixtures thereof. The personal care agents may be present in amounts which do not significantly adversely affect the properties and characteristics desired, such as from about 0.05 to about 50% by weight.

Suitable anionic surfactants include, but are not limited to, sodium lauryl sulfate, sodium lauryl ether sulfate, triethanolamine lauryl sulfate, sodium C₁₄₋₁₆ olefin sulfonate, ammonium pareth-25 sulfate (ammonium salt of a sulfated polyethylene glycol ether of a mixture of C₁₂₋₁₅ fatty alcohols), sodium myristyl ether sulfate, ammonium lauryl ether sulfate, disodium monooleamidodisulfosuccinate, ammonium lauryl sulfosuccinate, sodium dodecylbenzene sulfonate, triethanolamine dodecylbenzene sulfonate and sodium N-lauryl sarcosinate.

Suitable humectants include, but are not limited to, polyhydric alcohols, polyalkylene glycols, and alkylene polyols and their derivatives. Illustrative are propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, 1,2,6-hexanetriol, ethoxylated glycerin, propoxylated glycerin and mixtures thereof.

Generally, the polymers and/or copolymers of the present invention can be used in an amount of at least about 0.05 wt.%, preferably at least about 1 wt.%, and more preferably at least about 3 wt.% of the personal care composition. Generally, the polymers and/or copolymers of the present invention can be used in an amount of

at most about 50%, preferably at most about 30, and more preferably at most about 10 wt.% of the personal care composition.

The polymers and/or copolymers of the present invention are suitable for high water content emulsion products such as skin creams.

5 The polymers and/or copolymers used in accordance with the invention are particularly effective in personal care composition because of good oxidative stability due to selective hydrogenation, i.e., there is no tendency to turn rancid. Controlled product viscosity of the copolymers of the present invention also provides a variety of products suitable to different end uses. Optical clarity of the copolymers
10 allows for use in transparent and opaque formulations. The star-branched structure of the copolymers of the present invention allows for lower viscosity at a given molecular weight. Higher viscosity of the copolymers of the present invention than commercially available materials provides for better personal care product property retention. Good compatibility/solubility of personal care formulation components
15 allows for enhanced effectiveness of active ingredients.

 The composition of the present invention may be tailored in terms of refractive index within specific ranges depending on monomer composition. For example, copolymers containing polyisoprene, butadiene, and styrene may have refractive indices in the range of from about 1.470 to about 1.590 depending on the
20 monomers present and degree of unsaturation. By contrast, the refractive indices of polyisobutylenes are necessarily from 1.505-1.510.

Refractive Indices:

	Unhydrogenated	
5	Polyisoprene	1.521
	Polybutadiene	1.500-1.518
	Polystyrene	1.590-1.592
	Hydrogenated	
	Polyalphaolefins	1.480-1.490
10	Diene-based copolymers	1.470-1.480
	of the present invention	
	For comparison	
	Polyisobutylene	1.505-1.51

15 Examples

The following examples are intended to assist in a further understanding of the invention. The particular materials and conditions employed are intended to be further illustrative of the invention and are not limiting upon the reasonable scope thereof.

In all of the following examples, the experimental polymerization and functionalization work was performed with dried reactors and equipment and under strictly anaerobic conditions. All percentages are by weight. Extreme care must be used to exclude air, moisture and other impurities capable of interfering with the delicate chemical balance involved in the synthesis of the polymers of this invention, as will be apparent to those skilled in the art.

Example I: **Preparation of Polymer Precursor Backbones**

Using the procedure described in Example VII of U.S. Patent 5,633,415,
5 incorporated herein by reference, an isoprene-butadiene diblock polymer having a
number average molecular weight of about 15,000 is prepared.

Example II: **Selective Hydrogenation of the Polymer of Example I**

10 The polymer solution of Example I is subjected to a selective hydrogenation
procedure using a catalyst prepared by diethylaluminum ethoxide and cobalt octoate
(3.5 to 1 molar ratio) and following general procedures as described in Example VIII
of U.S. Patent 5,633,415, incorporated herein by reference. The extent of
hydrogenation is followed by Fourier Transfer Infrared (FTIR) and is continued until
15 no absorption remains at 910 cm^{-1} and 990 cm^{-1} (-1,2 polybutadiene structure) and
essentially no residual trans double bonds are present as seen by disappearance of the
968 cm^{-1} absorption. The FTIR analysis of the polymers at the end of the selective
hydrogenation typically indicates 0 to 10 trans polybutadiene double bonds and 50 to
100 vinylidene (-3,4 polyisoprene) double bonds remain - normalized to 100,000
20 molecular weight polymer chain. The polymer of Example I has 0 to 1.5 trans double
bonds and 7.5 to 15 vinylidene double bonds (for subsequent functionalization).

The hydrogenation catalyst is removed by washing, as described in U.S.
5,633,415, or by a filtration procedure preceded by precipitation of the catalyst with
essentially stoichiometric levels of acetic acid and hydrogen peroxide. After catalyst
25 removal, the solvent is removed under reduced pressure to give the selectively
hydrogenated polymer.

Example III: **Bodywash Formulation Containing the Polymer of Example II**

The following bodywash formulation is prepared using the IB copolymer of Example II:

5

BODY WASH with Liquid Isoprene-Butadiene Copolymer

	<u>PHASE</u>	<u>INGREDIENT</u>	<u>WT%</u>
	A	Deionized water	28.05
10	A	Chelating Agent	0.10
	A	Stabilizer and Thickener	10.00
	B	Anionic Surfactant	25.00
	C	Anionic Surfactant	25.00
	D	Foaming Agent and Stabilizer	2.00
15	E	<i>Liquid IB Copolymer</i>	1.00
	E	Stabilizer and Emulsifier	3.00
	E	Pearlizer	2.00
	F	Thickener and Foaming Agent	3.00
	G	Fragrance	0.40
20	H	Preservative	0.25
	I	Blue Color	0.20

Manufacturing Instructions

1. Heat phase A to 75 °C.
2. Add phases B, C, D, E & F.
3. Cool to 40 °C and add phases G, H & I.
4. Adjust pH to 5.5-6.5.
5. Adjust viscosity to 2,000-4,000 cPs with NaCl solution.

25

Product

A light blue body wash that provides a silky, long-lasting, and non-greasy skin feel.

5

Example IV: Night Cream Formulation Containing the Polymer of Example II

The following night cream formulation is prepared using the IB copolymer of Example II:

NIGHT CREAM with Liquid Isoprene-Butadiene Copolymer

	<u>PHASE</u>	<u>INGREDIENT</u>	<u>WT%</u>
5	A	Deionized water	67.05
	A	Thickener	10.00
	A	Emulsifier	0.20
	A	Humectant	3.00
10	B	Emulsifier	2.00
	B	Shea butter	5.00
	B	Emollient	1.00
	B	Stabilizer	0.25
	B	Synthetic ester fluid	4.00
15	B	<i>Liquid IB Copolymer</i>	3.50
	B	Antioxidant	0.25
	B	Emulsifier	2.00
	C	pH Neutralizer	0.50
	D	Fragrance	0.25
20	E	Preservative	1.00

Manufacturing Instructions

1. Heat phase A to 75 °C.
2. Heat phase B to 75 °C.
- 25 3. Add phase B to phase A.
4. Add phase C.
5. Cool to 45 °C and add remaining phases.

Product

A smooth, non-greasy night cream. The liquid IB copolymer of Example II provides the final skin feel emollient properties.

5 Example V: **Hair Conditioner Formulation Containing the Polymer of Example II**

The following hair conditioner formulation is prepared using the IB copolymer of Example II:

10 HAIR CONDITIONER with Liquid Isoprene-Butadiene Copolymer

	<u>PHASE</u>	<u>INGREDIENT</u>	<u>WT%</u>
	A	Deionized water	85.21
15	A	Conditioner	1.10
	A	Conditioner and Emulsifier	3.00
	A	Humectant	1.00
	A	Wetting Agent	0.10
	B	Thickener	2.00
20	B	Non-ionic Emulsifier	0.50
	B	Antioxidant	0.10
	B	Conditioner	5.20
	B	<i>Liquid IB Copolymer</i>	0.20
	B	Synthetic ester fluid	0.80
25	C	Fragrance	0.35
	D	Preservative	0.20
	E	pH Adjuster	0.24

Manufacturing Instructions

1. Heat phase A to 75°C.
2. Heat phase B to 75°C.
3. Add phase B to phase A.
- 5 4. Add phase C.
5. Cool to 45°C and add remaining phases.

Product

A hair conditioner which imparts good conditioning and gloss to the hair.

- 10 The liquid IB copolymer of Example II provides the final feel and gloss. The conditioner has nice body and a lubricious skin feel.

Example VI: Preparation of Polymer Precursor Backbones

- 15 Using the procedure described in Example XVII of U.S. Patent 5,288,937, incorporated herein by reference, an isoprene-butadiene diblock polymer living polymer that is subsequently coupled to yield branched materials and having a number average molecular weight of about 32,000 is prepared.

20 **Example VII: Selective Hydrogenation of the Polymer of Example VI**

- The polymer solution of Example VI is subjected to a selective hydrogenation procedure using a catalyst prepared by diethylaluminum ethoxide and cobalt octoate (3.5 to 1 molar ratio) and following general procedures as described in
- 25 Example VIII of U.S. Patent 5,288,937, incorporated herein by reference. The extent of hydrogenation is followed by Fourier Transfer Infrared (FTIR) and is continued until no absorption remains at 910 cm^{-1} and 990 cm^{-1} (-1,2 polybutadiene structure) and essentially no residual trans double bonds are present as seen by disappearance of the 968 cm^{-1} absorption. The FTIR analysis of the polymers at the end of the

selective hydrogenation typically indicates 0 to 10 trans polybutadiene double bonds and 50 to 100 vinylidene (-3,4 polyisoprene) double bonds remain - normalized to 100,000 molecular weight polymer chain. The polymer of Example I has 0 to 1.5 trans double bonds and 7.5 to 15 vinylidene double bonds (for subsequent functionalization).

The hydrogenation catalyst is removed by washing, as described in U.S. 5,288,937, or by a filtration procedure preceded by precipitation of the catalyst with essentially stoichiometric levels of acetic acid and hydrogen peroxide. After catalyst removal, the solvent is removed under reduced pressure to give the selectively hydrogenated polymer.

Example VIII: Preparation of Polymer Precursor Backbones

Using the procedure described in Example VII of U.S. Patent 5,633,415, incorporated herein by reference, an isoprene-butadiene diblock polymer having a number average molecular weight of about 10,000 is prepared.

Example IX: Selective Hydrogenation of the Polymer of Example VIII

The polymer solution of Example VIII is subjected to a selective hydrogenation procedure using a catalyst prepared by diethylaluminum ethoxide and cobalt octoate (3.5 to 1 molar ratio) and following general procedures as described in Example VIII of U.S. Patent 5,633,415, incorporated herein by reference. The extent of hydrogenation is followed by Fourier Transfer Infrared (FTIR) and is continued until no absorption remains at 910 cm^{-1} and 990 cm^{-1} (-1,2 polybutadiene structure) and essentially no residual trans double bonds are present as seen by disappearance of the 968 cm^{-1} absorption. The FTIR analysis of the polymers at the end of the selective hydrogenation typically indicates 0 to 10 trans polybutadiene double bonds and 50 to 100 vinylidene (-3,4 polyisoprene) double bonds remain - normalized to

100,000 molecular weight polymer chain. The polymer of Example I has 0 to 1.5 trans double bonds and 7.5 to 15 vinylidene double bonds (for subsequent functionalization).

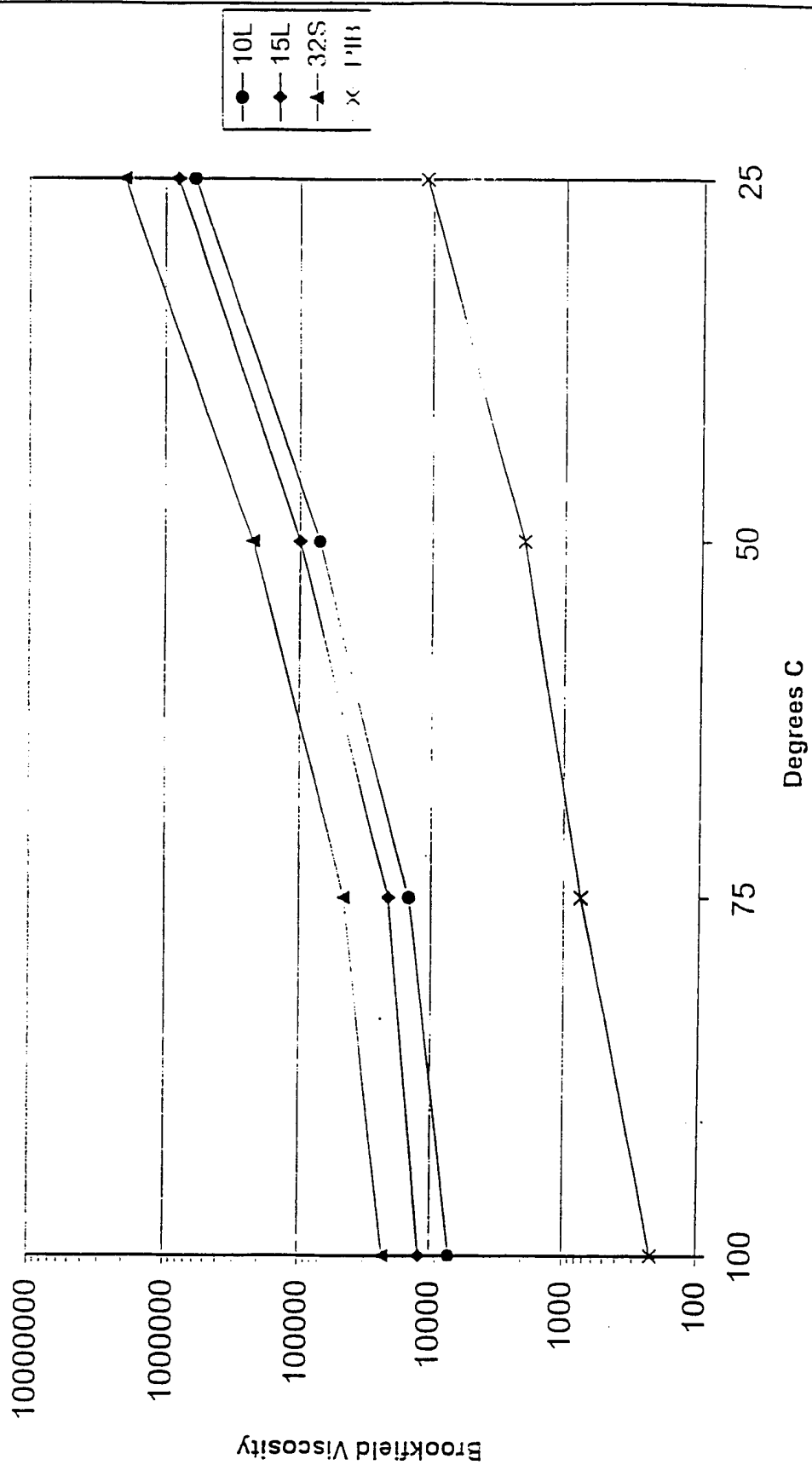
5 The hydrogenation catalyst is removed by washing, as described in U.S. 5,633,415, or by a filtration procedure preceded by precipitation of the catalyst with essentially stoichiometric levels of acetic acid and hydrogen peroxide. After catalyst removal, the solvent is removed under reduced pressure to give the selectively hydrogenated polymer.

10

Example X

The Brookfield viscosities of the polymers of Examples II, VI, VIII and polyisobutylene are shown in the following TABLE 1.

TABLE 1

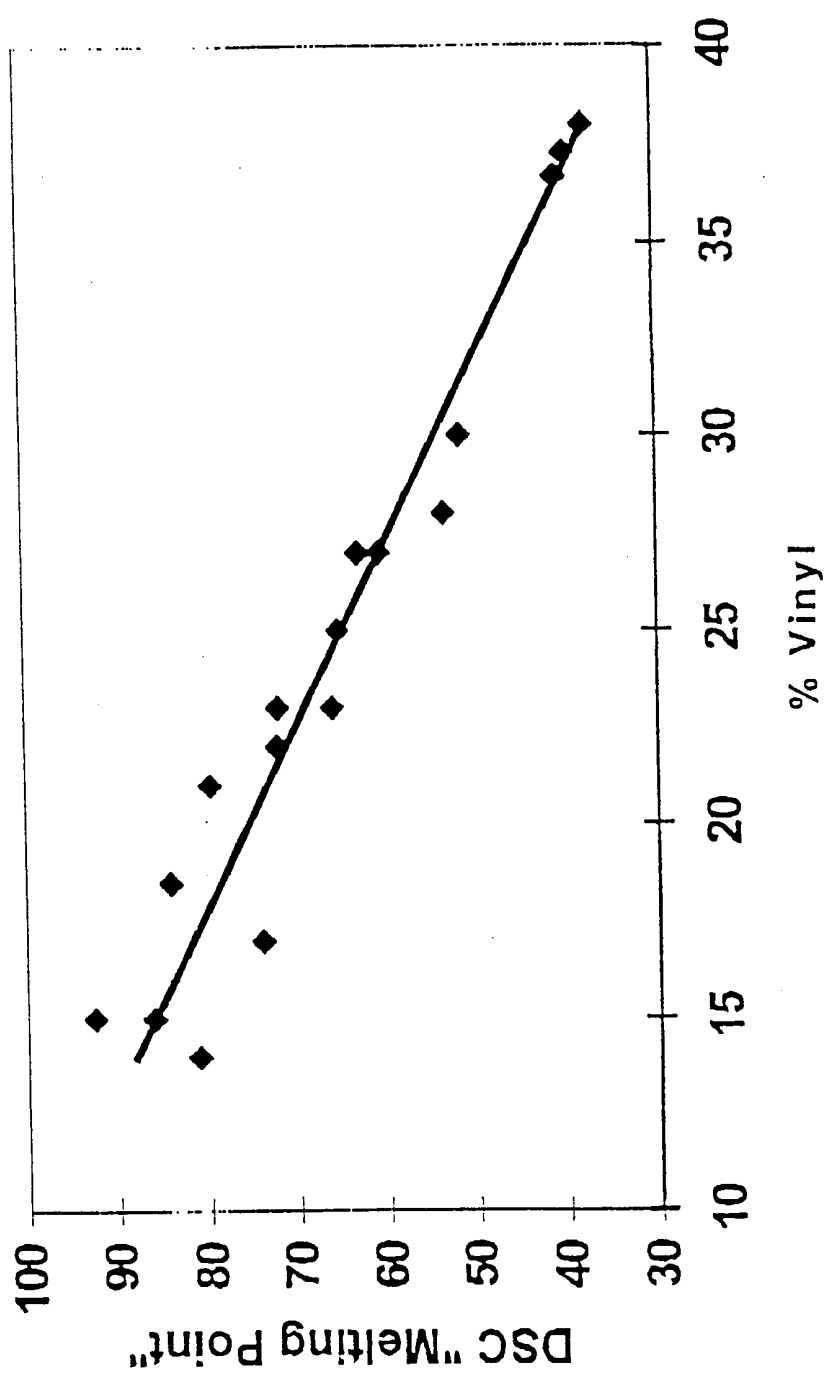


Depending on molecular weight and temperature, a wide range of polymer viscosities are attainable in a highly repeatable manner using the polymers and/or copolymers of the present invention, as compared to PIB. A narrow polydispersity (M_w/M_n) provides for materials with lower viscosity for a given molecular weight than other polymers prepared by means other than anionic polymerization, e.g., Ziegler-Natta or free radical methods

Example XI

The melting points of several polymers of this invention all having a molecular weight of 10,000 and with varying vinyl content are shown in TABLE 2.

TABLE 2



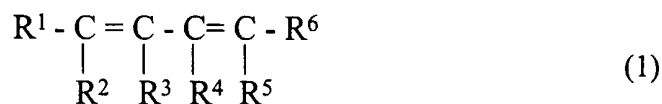
The data show a linear correlation between the vinyl content of the polymer and the melting point as determined by differential scanning calorimetry (DSC). At relatively low vinyl content, polymers of this invention upon selective hydrogenation
5 display a broad melting point range, from about 30-90°C. It is believed that this allows formulators an additional degree of freedom not available with traditional polymers, such as polyisobutylene which exists as amorphous fluid at low molecular weight..

It will be apparent to those skilled in the art that the specific embodiments
10 discussed above can be successfully repeated with ingredients equivalent to those generically or specifically set forth above and under variable process conditions. From the foregoing specification, one skilled in the art can readily ascertain the essential features of this invention and without departing from the spirit and scope thereof can adapt it to various diverse applications.

15 Thus, while there have been described what are presently believed to be the preferred embodiments of the present invention, those skilled in the art will realize that other and further embodiments can be made without departing from the spirit of the invention, and it is intended to include all such further modifications and changes as come within the true scope of the claims set forth herein.

WHAT IS CLAIMED:

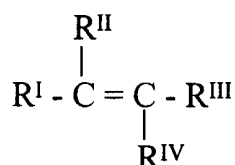
1. A personal care composition having film forming properties comprising a selectively hydrogenated polymer and/or copolymer selected from the group consisting of isoprene, butadiene, styrene or mixtures thereof; water and at least one personal care agent.
2. The personal care composition according to claim 1, wherein said selectively hydrogenated polymer and/or copolymer is in an amount in the range of from about 0.05 to about 50 wt.% based on the total weight of the personal care composition.
3. The personal care composition of claim 1, wherein said selectively hydrogenated polymer and/or copolymer is in an amount in the range of from about 1 to about 30 wt.% based on the total weight of the personal care composition.
4. The personal care composition of claim 1, wherein said selectively hydrogenated polymer and/or copolymer is in an amount in the range of from about 3 to about 10 wt.% based on the total weight of the personal care composition.
5. A personal care composition having water resistant properties comprising a copolymer of a first conjugated diene and a second conjugated diene, wherein:
said first conjugated diene comprises at least one relatively more substituted conjugated diene having at least five carbon atoms and the formula:



wherein R^1 - R^6 are each hydrogen or a hydrocarbyl group, provided that at least one of R^1 - R^6 is a hydrocarbyl group, provided that after polymerization, the unsaturation of the polymerized conjugated diene of formula (1) has the formula:

5

(2)

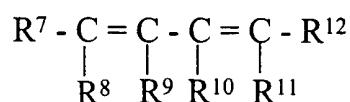


10

wherein R^I , R^{II} , R^{III} and R^{IV} are each hydrogen or a hydrocarbyl group, provided that either both R^I and R^{II} are hydrocarbyl groups or both R^{III} and R^{IV} are hydrocarbyl groups; and

said second conjugated diene comprises at least one relatively less substituted conjugated diene different from the first conjugated diene and having at least four carbon atoms and the formula:

(3)

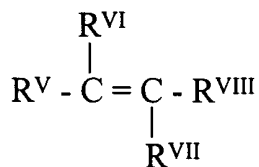


20

wherein R^7 - R^{12} are each hydrogen or a hydrocarbyl group, provided that after polymerization, the unsaturation of the polymerized conjugated diene of formula (3) has the formula:

25

(4)



wherein R^V , R^{VI} , R^{VII} and R^{VIII} are each hydrogen or a hydrocarbyl group,
provided that one of R^V or R^{VI} is hydrogen, one of R^{VII} or R^{VIII} is hydrogen, and at
5 least one of R^V , R^{VI} , R^{VII} and R^{VIII} is a hydrocarbyl group.

and wherein said copolymer has been selectively hydrogenated to provide a
selectively hydrogenated copolymer.

6. The personal care composition of claim 5, wherein said first
10 conjugated diene and said second conjugated diene are polymerized as a branched or
star-branched copolymer.

7. The personal care composition of claim 5, wherein said first
conjugated diene and said second conjugated diene are polymerized as a block,
15 tapered block or random copolymer.

8. The personal care composition of claim 5, wherein said copolymer has
a molecular weight in the range of from about 2,000 to about 100,000.

20 9. The personal care composition of claim 5, wherein said copolymer has
a molecular weight in the range of from about 3,000 to about 50,000.

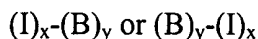
10. The personal care composition of claim 5, wherein said copolymer has
a molecular weight in the range of from about 5,000 to about 35,000.

11. The personal care composition of claim 5, wherein said selectively hydrogenating step provides a selectively hydrogenated copolymer wherein the unsaturation in formula (4) is substantially completely hydrogenated to retain substantially none of the original unsaturation, while unsaturation of formula (2)
5 retains a sufficient amount of its original unsaturation.

12. The personal care composition of claim 5, wherein the conjugated diene of formula (1) comprises isoprene, 2,3-dimethyl-butadiene, 2-methyl-1,3-pentadiene, myrcene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-phenyl-
10 1,3-butadiene, 2-phenyl-1,3-pentadiene, 3-phenyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-hexyl-1,3-butadiene, 3-methyl-1,3-hexadiene, 2-benzyl-1,3-butadiene, 2-p-tolyl-1,3-butadiene, or mixtures thereof.

13. The personal care composition of claim 5, wherein the conjugated
15 diene of formula (3) comprises 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, 1,3-hexadiene, 1,3-heptadiene, 2,4-heptadiene, 1,3-octadiene, 2,4-octadiene, 3,5-octadiene, 1,3-nonadiene, 2,4-nonadiene, 3,5-nonadiene, 1,3-decadiene, 2,4-decadiene, 3,5-decadiene, or mixtures thereof.

20 14. The personal care composition of claim 5, wherein said first and second conjugated dienes are polymerized as a block copolymer comprising at least two alternating blocks:



wherein:

25 the block (I) comprises at least one polymerized conjugated diene of formula (1);

the block (B) comprises at least one polymerized conjugated diene of formula (3);

x is the number of polymerized monomer units in block (I) and is at least 1,
and

y is the number of polymerized monomer units in block (B) and is at least 25.

5 15. The personal care composition of claim 5, wherein said conjugated diene of formula (3) comprises 1,3 butadiene and each of the (B) blocks is a mixture of 1,4- and 1,2- units.

10 16. The personal care composition of claim 15, wherein block (B), block (I) or both blocks (B) and (I), further comprises an aryl-substituted olefin.

15 17. The personal care composition of claim 16, wherein said aryl-substituted olefin comprises styrene, alkylated styrene, vinyl naphthalene, alkylated vinyl naphthalene, or mixtures thereof.

 18. The personal care composition of claim 1, in the form of a night cream wherein said at least one personal care agent is a humectant.

20 19. The personal care composition of claim 1, in the form of a bodywash wherein said at least one personal care agent is an anionic surfactant.

 20. The personal care composition of claim 1, in the form of a hair conditioner wherein said at least one personal care agent is a conditioning agent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/27810

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/48

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)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, CHEM ABS Data, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 461 497 A (BASF AG) 18 December 1991 (1991-12-18) claims 1-4; example 1 ----	1-4
X	US 4 122 023 A (YASUI SEIMEI ET AL) 24 October 1978 (1978-10-24) claims 1-13; examples 5-7 ----	1-4
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 337 (C-1217), 27 June 1994 (1994-06-27) & JP 06 080856 A (KURARAY CO LTD), 22 March 1994 (1994-03-22) abstract ----	
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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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

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G document member of the same patent family

Date of the actual completion of the international search

9 February 2001

Date of mailing of the international search report

19/02/2001

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INTERNATIONAL SEARCH REPORT

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