

IMPROVED VISCOSITY MODIFIER POLYBUTADIENE POLYMERSBACKGROUND OF THE INVENTION

5

FIELD OF THE INVENTION

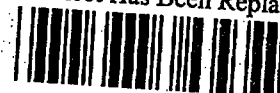
The present invention relates to hydrogenated polybutadiene comprising monomeric units of 1,4-butadiene and 1,2-butadiene addition products. More particularly, it relates to polybutadiene comprising hydrogenated blocks or segments of monomeric units of 1,2-butadiene and 1,4-butadiene addition products containing at least one crystallizable segment or block comprising an average of at least about 10 weight percent of the total hydrogenated copolymer chain, and at least one low crystallinity segment or block. The instant invention also relates to oleaginous compositions containing said copolymers as viscosity index improver additives, a process for making these copolymers and a method to control the viscosity of oleaginous compositions.

DESCRIPTION OF RELATED ART

Various copolymers of butadiene with other olefins are known to be used as oil additives. These include hydrogenated copolymers of butadiene with another conjugated diene such as isoprene. The copolymers are disclosed to be random or block copolymers. The following review of the related art illustrates attempts which have been made to develop hydrogenated butadiene base copolymers for use as an oil additive including a viscosity modifier.

SUBSTITUTE SHEET

This Sheet Has Been Replaced



-2-

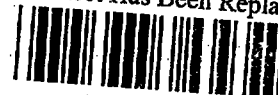
U. S. Patent No. 4,804,794 discloses segmented copolymers of ethylene and at least one other α -olefin monomer. Each copolymer is intramolecularly heterogeneous and intramolecularly homogeneous. At least one segment of the copolymer constituting at least 10% of the copolymer chain, is a crystallizable segment. The remaining segments of the copolymer chain are termed low crystallinity segments, and are characterized by an ethylene content of not greater than about 53 weight percent.

The α -olefin can include those containing 3 to 18 carbon atoms. α -olefins having 3 to 6 carbon atoms are indicated to be preferred. With the most preferred copolymers being copolymers of ethylene with propylene or ethylene with propylene and diene. The copolymers are disclosed to improve the properties in oleaginous fluids, in particular lubricating oil.

U. S. Patent No. 3,419,365 discloses hydrogenated copolymers of butadiene and styrene as pour point depressants for distillate fuel oil; U. S. Patent No. 3,393,057 discloses polymers of butadiene C10 to C24 normal alpha-monoolefins and styrene or indene as pour point depressants for fuel and lubricating oils; and U. S. Patent No. 3,635,685 discloses pour point depressants comprising hydrogenated butadiene-styrene copolymers which contain a hydroxy, carboxy, or pyridyl terminal group.

U. S. Patent No. 3,312,621 discloses polymers of conjugated diolefins which are predominantly in the 1,4-addition configuration, as viscosity index (V.I.) improvers. Butadiene, isoprene, 1,3-pentadiene, and copolymers of such diolefins are specifically disclosed as suitable.

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-3-

U. S. Patent No. 3,600,311 discloses viscosity index improvers of hydrogenated homopolymers of butadiene in which about 45 to 95 % of the butadiene monomers are in the 1,4-configuration.

5 U. S. Patent No. 3,795,615 discloses viscosity index improvers of hydrogenated copolymers of butadiene with a different conjugated diene, e.g., isoprene in which the monomer units in the polymer are predominantly in the 1,4-configuration. This patent
10 discloses that hydrogenated 1,4-polybutadiene is not useful as a viscosity index improver, since the final product is an oil-insoluble polyethylene. Hydrogenated polybutadienes with an appropriate amount of 1,2-structure would give the necessary solubility and would
15 have viscosity index improving properties. However, this references teaches that it is necessary to very precisely control the amount of 1,2-structure formed. If an inadequate amount of 1,2-structure is formed, the polymer is not sufficiently soluble; if too much 1,2-
20 structure is formed, the polymer is not as effective in increasing the viscosity index. The patent further discloses that when polybutadiene is anionically polymerized to the high degree of polymerization needed for viscosity index improvers , it is very difficult to
25 obtain precise control of the amount of 1,2-addition product by variations in reaction conditions.

U. S. Patent No. 3,965,019 discloses hydrogenated random, tapered or block copolymers of butadiene and isoprene to be useful as viscosity modifiers.

30 U. S. Patent No. 4,032,459 discloses a viscosity index improver comprising a copolymer of butadiene and isoprene having between 20-55% 1,4-configuration, this

SUBSTITUTE SHEET

This Sheet Has Been Replaced



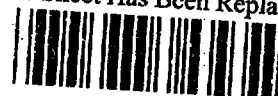
-4-

polymer then having been hydrogenated to remove substantially all of the olefinic unsaturation.

U. S. Patent No. 4,073,737 discloses viscosity index improver comprised of a hydrogenated copolymer produced by copolymerization of from about 1 to about 10 mole percent butadiene, at least one other C5 to C12 conjugated diene, and up to 45 mole percent of a vinyl aromatic monomer.

A useful class of viscosity index improvers for lube oil compositions are star-shaped polymers comprising a nucleus such as divinylbenzene with polymeric arms linked to it. Such polymers are disclosed in patents, such as U. S. Patent No. 4,358,565 and 4,620,048. Generally star-shaped polymers are disclosed to be formed by polymerizing one or more conjugated dienes and optionally, one or more monoalkenylarene compound in solution in the presence of an ionic initiator to form a living polymer. For the purpose of the present invention the term "living polymer" is used consistent with Billmeyer, Textbook of Polymer Science, 2d Ed., page 348, Wiley-Interscience, John Wiley and Sons, page 318 (1971). Specific conjugated dienes include conjugated dienes having 4 to 12 carbon atoms and optionally, one or more monoalkenylarene compounds. Typical and useful conjugated dienes include butadiene (1,3-butadiene) and isoprene. The living polymers thereby produced are then reacted with a polyalkenyl coupling agent to form star-shaped polymers. The coupling agents have at least two non-conjugated alkenyl groups. The groups are usually attached to the same or different electron drawing groups, e.g., an aromatic nucleus. Such compounds have the property that at least two of the alkenyl groups are capable of independent reaction with

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-5-

different living polymers, and in this respect, are different from conventional dienes polymerizable monomers, such as butadiene and isoprene. The coupling agents may be aliphatic, aromatic or heterocyclic.

5 Examples of aliphatic compounds include polyvinyl and polyallyl acetylenes, diacetylenes, phosphates, and phosphites, as well as the dimethacrylates, e.g., ethyl dimethacrylate. Examples of suitable heterocyclic

10 compounds include divinyl pyridine and divinyl thiophene. Coupling agents disclosed to be preferred in the U. S. Patent No. 4,358,565 patent are polyalkenyl aromatic compounds with the most preferred being indicated to be polyvinyl aromatic compounds.

15 Examples of such compounds include those aromatic compounds, e.g., benzene, toluene, xylene, anthracene, naphthalene, and durene which are substituted by at least two alkenyl groups, preferably directly attached thereto. Specific examples include polyvinyl benzenes, e.g., divinyl, trivinyl, and tetravinyl benzenes;

20 divinyl, trivinyl and tetravinyl, ortho, meta and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropanol benzene, and diisopropanol biphenyl. The polyalkenyl coupling agent should be added to the living polymer
25 after the polymerization of the monomers is substantially complete, i.e., the agent should only be added after substantially all of the monomer has been converted to living polymer.

30 The amount of polyalkenyl coupling agent added may vary, but preferably, at least 0.5 moles is used per mole of unsaturated living polymer. Amounts from 1 to 15 moles, and preferably 1.5 to 5 moles are preferred.

There exists a need for viscosity index improvers which, when added to oleaginous compositions, such as

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-6-

lube oil compositions, yield compositions exhibiting better or improved low temperature viscometric characteristics than are obtainable by the use of conventional viscosity index improver additives. The copolymers of the instant invention provide oleaginous compositions exhibiting such improved low temperature viscometric characteristics, and additionally, improved shear stability.

For convenience, certain terms that are repeated throughout the present specification and claims are defined below.

a. Viscosity Index (V.I.) is the ability of a lubricating oil to accommodate increase in temperature with a minimum decrease in viscosity. The greater this ability, the higher the V.I.

b. A block copolymer is a copolymer having at least one sequence (also referred to as block or segment) of the same monomer units. Each sequence has at least two monomer units. Block copolymers typically have a plurality of each type of monomer making up the copolymer. The terms relating to block copolymer are consistent with those given in Billmeyer, Jr., Textbook of Polymer Science, Second Edition, Wiley-Interscience (1971). For the purpose of the present invention the term block or segmented copolymer includes a copolymer comprising monomeric units of 1,2-butadiene and 1,4-butadiene.

c. Average methylene content of a segment of the hydrogenated copolymer is the average number of methylene moieties or units present in the segment. The methylene units are those present in the particular segment as a result of the polymerization and

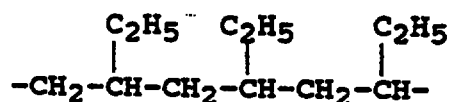
This Sheet Has Been Replaced



SUBSTITUTE SHEET

-7-

hydrogenation of butadiene and at least one other conjugated diene, such as isoprene. Thus, for example, the hydrogenation product of the 1,4-addition product of two 1,4-butadiene molecules contains one methylene segment comprised of eight methylene units and has a methylene content of 100%, i.e., $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$. The hydrogenation product of the 1,2-addition product of 1,2-butadiene contains one methylene units alternating with an ethylene substituted methylene unit, i.e.,



The following defines how percent methylene units are calculated from the percentages of hydrogenated 1,2 and 1,4 polybutadiene in the polymer. Each enchainment 1,4-butadiene ($B_{1,4}$) unit contributes four methylenes. Each 1,2-butadiene contributes one methylene and one substituted methylene. Where B represents the mole fraction 1,4-butadiene then $(1-B)$ is the fraction 1,2-butadiene. The mole fraction methylenes present, X_{CH_2} is then

$$X_{\text{CH}_2} = \frac{3 B_{1,4} + 1}{2 B_{1,4} + 2} \quad (1)$$

where $B_{1,4}$ is the fraction of 1,4-addition of butadiene. For $B_{1,4} = 1$, $X_{\text{CH}_2} = 1$. For all 1,2-addition $X_{\text{CH}_2} = 0.5$, but there can be no long methylene sequences.

To obtain crystallizable sequences there must be sequences of 1,4 enchainment units. For random addition of 1,2-butadiene and 1,4-butadiene units $B_{1,4}$ is approximately 0.3 or 30 percent to obtain



-8-

crystallinity. From formula (1) $X_{CH_2} = .73$ at $B_{1,4} = .3$. In principle, if the statistical distribution of 1,2 and 1,4-butadiene additions is of a block type, than random crystallinity could occur at $B_{1,4}$ below .3.

5 In all cases where sequences of methylenes are long enough to crystallize at least two adjacent hydrogenated 1,4-butadiene units are present, and generally 3 or more are present. In such cases, methylenes from 1,2-butadiene becomes less important
10 for crystallization since they add only one or two units to an 8 to 12 unit sequence. For purposes of the present invention the composition of crystallizable segments is in terms of 1,4-butadiene content, i.e., only those methylene segments contributed by 1,4-
15 butadiene units are counted

d. By "crystallize" it is meant that the methylene sequences in the polymer associate into ordered state consistent with the classical definition of polymer crystallinity as set forth, for example, by
20 Flory, Principles of Polymer Chemistry, Cornell University Press (1953).

e. Crystallizable units are defined as methylene groups in sequence which exhibit a heat of fusion when measured by differential scanning calorimetry (DSC)
25 upon cooling from the melt. In a procedure useful for the present invention a sample can be formed into an approximately 0.030 inch thick sheet for 30 minutes at 150°C and then annealed at 20°C for 48 hours prior to measurement, loaded into the calorimeter at that
30 temperature, rapidly cooled to -100°C and scanned to 150°C at 20°C/minute. Only sequences melting between 20°C and 140°C are included.

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-9-

f. The weight percent crystallizable units is:

$$\frac{\text{Heat of fusion measured cal/gm}}{69 \text{ cal/gm}} \cdot 100.$$

5 On this basis pure melt crystallized polymethylene
of high Mw (i.e., where the end groups effects are not
significant; typically greater equal or about 20,000)
has about 60% crystallizable units. Kinetic
restrictions prevent them from all crystallizing.
10 Percent crystallinity can be measured by a techniques,
as defined in G. Ver Strate, Z. W. Wilchinsky, J. Pol.
Sci. Physics, A2, 9, 127 (1971), which is incorporated
herein by reference. The degree of crystallinity
measured is a function of the sample's annealing
15 history. Some low amount is desirable in this product
when the sample is annealed at 20°C. for more than 48
hours after preparation of a void-free, strain-free
specimen by heating to 150°C. for 30 minutes in a
suitable mold. Crystallizability also depends on other
20 factors: temperature, diluent, and the composition of
the copolymer.

g. The association temperature (T_a), is the
temperature at which crystallization of the copolymer
of the present invention can be determined by studying
25 the temperature dependance of the relative viscosity
(η_{rel}). Deviation from an established ($d\eta_{rel}/dT$) trend
occurs when significant association at polymer segments
due to crystallinity starts. (ASTM method D-445 for
kinematic viscosity can be run at a series of
30 temperatures. The polymer concentration in these
measurements should be the same as that in the
formulated oil, for example, 1%).

h. The cloud point temperature is the
temperature (T_c) at which crystalline clouds

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-10-

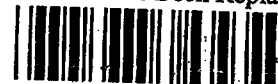
(turbidity) are first observable upon cooling of oil when tested according to ASTM D-2500. The cloud point temperature can be correlated with the association temperature.

5 i. A crystallizable segment of the hydrogenated
copolymer chain is rich in methylene units, with an
average methylene content of at least about 75 mole
percent. The methylene content depends on the monomers
10 inclusion in the polymer. The methylene units will
crystallize at a given temperature and concentration in
solution only if they are in long enough sequences,
with only a limited number of interruptions due to
substituted methylene units. More interruptions are
15 acceptable with methyl substitutions than with larger
groups since methyl groups can enter the polymethylene
crystal lattice. Methylene units can be identified by
C₁₃ NMR, T. Hayashi, Y. Iroue, R. Chujo,
Macromolecules, 21, 3139, 1988, and references therein.
20 Sequences of 5 or more cannot be distinguished.
However units are actually crystallizable only if they
are present in sequences of about 13 methylenes or
longer.

25 j. A low crystallinity segment has an average
methylene content less than about 75 mole percent, and
is characterized in the unoriented bulk state after at
least 24 hours annealing by a degree of crystallinity
of less than about 0.2% at 23°C.

30 k. Molecular weights of the hydrogenated
copolymer were measured by a combination of gel
permeation chromatography and on line laser light
scattering and described in G. Ver Strate, C. Cozewith,
S. Ju, Macromolecules, 21, 3360, 1989. The specific

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-11-

refractive index increment in trichlorobenzene at 135°C. was assumed to be -0.104 cc/g for all hydrocarbon structures.

SUMMARY OF THE INVENTION

5 The present invention is directed to a hydrogenated block copolymer, a process to make the copolymer, compositions containing the copolymer and methods to use the copolymer.

10 The hydrogenated block copolymer of the preset invention comprises a hydrogenated block copolymer comprising monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products of the polymerization of butadiene. The copolymer is hydrogenated and comprises at least 10 weight percent
15 by weight of at least one crystallizable segment comprised of methylene units. Correspondingly, the crystallizable segment has an average 1,4-polybutadiene the content of at least about 20 mole percent and preferably at least 30 mole percent. The block
20 copolymer has at least one low crystallinity segment comprised of methylene units and substituted methylene units and has an average 1,4-polybutadiene content of not greater than 20 mole percent and preferably less than 10 mole percent. The 1,4-butadiene and 1,2-
25 butadiene units are present in amounts effective to provide at least one crystallizable segment and at least one low crystallinity segment. A preferred block copolymer is where the copolymer is in star copolymer form having from 4 to 25 and preferably 5 to 15 arms.

30 Preferably, the crystallizable segments have a number average molecular weight of at least 500. The average 1,4-polybutadiene content is at least 20 mole

This Sheet Has Been Replaced



SUBSTITUTE SHEET

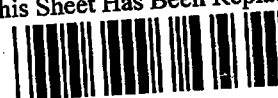
-12-

percent and preferably at least 50 percent of the methylene units are connected in series of at least 13 adjacent methylene units in length. The remaining segments of the copolymer chain are the low
5 crystallinity segments preferably having an average 1,4-polybutadiene content of less than about 20 mole percent.

The present invention includes compositions comprising oleaginous compounds and the above recited
10 hydrogenated block copolymer. Preferably the oleaginous component is an oil composition comprising oil, such as lubricating oil. Typically, the oleaginous composition comprises from 0.1 to 50, preferably from 0.05 to 25 percent by weight of the
15 hydrogenated copolymer of the present invention. Preferred compositions of the present invention comprise copolymer as recited above having a crystallization temperature (T_a) and oil having a cloud point temperature (T_c), where (T_a) is greater than
20 (T_c). The lubricating oil compositions can contain additional additives, such as other viscosity modifiers, ashless dispersants, antioxidants, corrosion inhibitors, detergents, pour point depressants, anti-wear agents, and the like.

25 The copolymers have been found to impart excellent low temperature viscometric properties to oleaginous fluids, particularly lubricating oils. The compositions have satisfactory viscosities at room temperatures and at higher temperatures. The
30 compositions of the present invention are useful for typical lubricating oil compositions such as automatic transmission fluids, heavy duty oil suitable for use in crankcases of gasoline and diesel engines, and any

This Sheet Has Been Replaced



-13-

machinery containing gears and power transmitting units.

The present invention additionally comprises a process to make the hydrogenated block copolymer recited above. The process comprises the steps of polymerizing a precursor block copolymer comprising at least one segment comprising at least 20 percent by mole of monomeric units of 1,4-butadiene, and at least one comonomer segment comprising comonomer units of 1,2-butadiene. The process further comprises substantially hydrogenating the precursor copolymer to form the above recited hydrogenated block copolymer. The process is preferably an anionic polymerization. In forming the precursor block copolymer the polymerization process preferably takes either of two approaches. The first is to first control the polymerization to form 1,4-butadiene segments, and then control the polymerization to form comonomer segments comprising at least 70, and preferably at least 75, and more preferably at least 80 mole percent of 1,2-butadiene monomeric units. Alternatively, the comonomer can first be polymerized to form a comonomer segments comprising at least 70, preferably at least 75, and more preferably at least 80 mole percent of 1,2-butadiene monomeric units. The polymerization is then controlled to form 1,4-butadiene segments. Upon completion of the polymerization of the 1,4-butadiene additional comonomer can be added and the polymerization then controlled to form comonomer segments comprising at least 75 mole percent of 1,2-butadiene monomeric units.

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-14-

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to hydrogenated block copolymers based on butadiene comprising monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products. The copolymer contains at least one crystallizable segment or block and at least one low crystallinity segment or block. The hydrogenated copolymers are made by the controlled polymerization of butadiene, preferably by addition polymerization. The polymerization results in a precursor block copolymer comprising at least one 1,4-butadiene segment and at least one comonomer segment comprising comonomer units derived 1,2-butadiene, the copolymer comprising at least 10 percent by weight of the 1,4-butadiene segments. The precursor copolymer is then hydrogenated to substantially saturate the olefinic bonds and to form a hydrogenated copolymer containing at least one crystallizable segment and at least one low crystallinity segment. The crystallizable segment comprises at least an average of about 10 weight percent of the hydrogenated copolymer chain and contains an average 1,4-polybutadiene content of at least about 20 mole percent, preferably at least about 30 mole percent. An adequate amount of the methylene units are joined in sequences containing at least about 13 methylene units to permit crystallization.

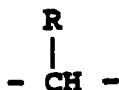
The low crystallinity segment has an average 1,4-polybutadiene content of less than 30 mole percent, preferably less than about 20 mole percent, and rich in substituted methylene units. The low-crystallinity segment correspondingly contains an average of at least about 22 mole percent, more preferably at least about 24 mole percent substituted methylene units. The

This Sheet Has Been Replaced



-15-

substituted methylene units from the 1,2-butadiene are represented by the formula



wherein R is an ethyl group.

The low crystallinity segment can contain, in addition to the hydrogenated 1,2-addition butadiene comonomer, hydrogenated 1,4-addition butadiene and minor amounts, i.e., from 0 to 5 mole percent, of other conjugated diene polymerization products. Such other conjugated dienes include those having from 5 to 24 carbon atoms. Thus, for example, the low crystallinity segment may contain the hydrogenated polymerization products of 1,2-butadiene, i.e., poly-1,2-butadiene, 1,4-butadiene, i.e., hydrogenated poly-1,4-butadiene, and isoprene, i.e., hydrogenated polyisoprene.

The copolymer may also optimally contain up to 5 mole percent of the hydrogenated polymerization product of other monomers such as, for example, monovinyl arenes such as styrene or substituted styrene methacrylates, vinyl pyridines or other anionically polymerizable monomers.

The size of the crystallizable segment which is present in the hydrogenated copolymer is in general dependent upon the relative amounts of 1,4-butadiene present in the precursor polymer. The crystallizable segment comprises at least about 10 weight percent, preferably from about 10 to about 90 weight percent, more preferably from about 20 to about 85 weight percent, and most preferably from about 40 to 65 weight

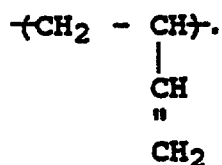
This Sheet Has Been Replaced



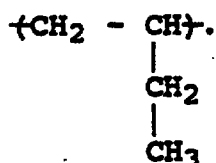
SUBSTITUTE SHEET

-17-

generated reaction products of 1,4-butadiene and 1,2-butadiene. The 1,4-configuration species predominate. The 1,2-addition of butadiene will yield a recurring structure represented by the formula



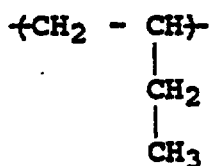
Hydrogenation of this structure results in a structure represented by the formula



Therefore, a hydrogenated copolymer of butadiene contains the following species:



obtained from the hydrogenation of 1,4-butadiene; and



obtained from the hydrogenation of 1,2-addition butadiene.

The recurring structural units other than those obtained by the hydrogenation of the 1,4-addition and 1,2-addition of butadiene may be present in both the crystallizable and low crystallinity segment. If they are present in the crystallizable segment, however, they are present in amounts which are insufficient to

This Sheet Has Been Replaced

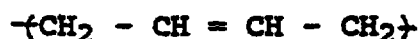


SUBSTITUTE SHEET

-18-

affect the crystallizable characteristics of said segment.

5 The crystallizable segments or blocks present in the hydrogenated copolymer are comprised predominantly of methylene units which are, inter alia, provided by the hydrogenation of the 1,4-butadiene present in the precursor copolymer. Thus, polymerizing butadiene monomer, i.e., $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, by 1,4-addition yields a precursor polymer segment containing recurring structural unit of the formula



15 Hydrogenating this precursor polymer chain yields a polymer segment containing the following recurring structural unit



20 i.e., containing only methylene units. This recurring structural unit, provided it is sufficiently long, e.g., contains at least about 13 methylene units, forms the crystallizable segment of the polymer chain.

25 Thus, there are two requirements that must be fulfilled in order for a segment to be crystallizable. The first requirement is that the segment have an average 1,4-polybutadiene content of at least about 20 mole percent, preferably at least about 30 weight percent (e.g., from about 20 to about 80 weight percent). The second is that the methylene units be in sequences sufficiently long to impart crystallinity to said segment. Generally, these sequences are at least 13 methylenes or longer, preferably at least 17 methylenes or longer, and more preferably at least 35 about 21 methylenes or longer.

SUBSTITUTE SHEET

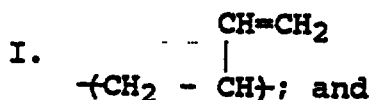
This Sheet Has Been Replaced



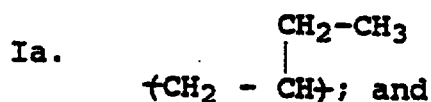
-19-

In a preferred copolymer of the instant invention there is at least about 20 mole percent of the butadiene in the 1,4-configuration in the precursor polymer. The precursor copolymer contains at least an amount of butadiene units in the 1,4-configuration sufficient to provide a hydrogenated copolymer containing at least one crystallizable segment comprising at least about 20 weight percent of said hydrogenated copolymer.

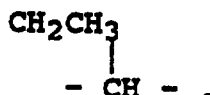
Polymerizing butadiene monomer by 1,2-addition and 1,4-addition yields a precursor polymer chain containing the following recurring structural units



Hydrogenating this precursor polymer yields a hydrogenated polymer chain containing the following recurring structural units



Recurring structural unit Ia contains one methylene unit and a substituted methylene unit, i.e.,



This Sheet Has Been Replaced

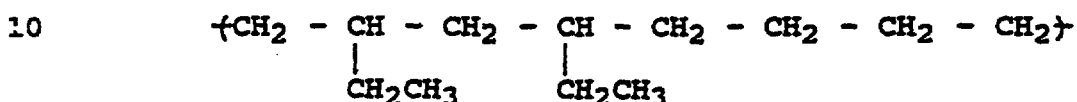


SUBSTITUTE SHEET

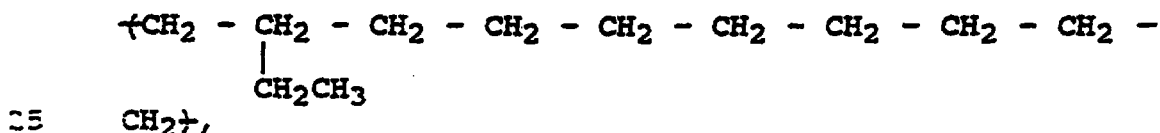
-20-

Where there are relatively large amounts of these substituted methylene moieties in a polymer segment, generally greater or equal to about 30 mole percent, the resulting hydrogenated polymer segment is a low crystallinity segment. The segment containing at least about 20 mole percent 1,4-polybutadiene units, and if these methylene segments are of sufficient length, is a crystallizable segment.

A segment containing the recurring unit



derived from the hydrogenation of the 1,2-addition product of two moles of butadiene for every mole of 1,4-butadiene, will generally not be a crystallizable segment because it is relatively rich in substituted methylene units, and the methylene sequences are not sufficiently long. A segment containing the recurring structural unit



derived from the hydrogenation of the 1,4-addition of two moles of butadiene for every mole of 1,2-butadiene, will be a crystallizable segment since it contains at least 30 mole percent 1,4-polybutadiene units, and since it contains uninterrupted methylene sequences containing at least about 13 methylene units.

The copolymers of this invention will contain at least one crystallizable segment rich in methylene units (hereinafter called an "M" segment) and at least

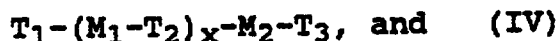
This Sheet Has Been Replaced



SUBSTITUTE SHEET

-21-

one low crystallinity segment relatively rich in substituted methylene units (hereinafter called a "T" segment). The copolymers may be therefore illustrated by copolymers selected from the group consisting of copolymer chain structures having the following segment sequences:



wherein M and T are defined above, M_1 and M_2 can be the same or different and are each M segments, T_1 , T_2 and T_3 can be the same or different and are each T segments, and x is an integer of from 0 to 3.

When $x=0$, the copolymer's M, i.e., M_2 segment is positioned between two T segments, and the M segment can be positioned substantially in the center of the polymer chain (that is, the T_1 and T_3 segments can be substantially the same molecular weight and the sum of the molecular weight of the T_1 and T_3 segments can be substantially equal to the molecular weight of the M_2 segment), although this is not essential to the practice of this invention. Preferably, the copolymer will contain only one M segment per chain. Therefore, structures III and IV ($x=0$) are preferred, with structure II being more preferred.

The preferred copolymer chain structures, from the standpoint of providing oleaginous compositions such as lube oil compositions have excellent low temperature viscometric properties.

Preferably, the M segments and T segments of the copolymer are located along the copolymer chain so that only a limited number of the copolymer chains can

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-22-

associate before the steric problems associated with packing the low crystallinity T segments prevents further agglomeration. Therefore, in a preferred embodiment, the M segment is located near the center of the copolymer chain and only one M segment is in the chain. In the case where x is one or larger it is important that the T₁ and T₃ segments be sufficiently large to prevent association of the M segments from different polymer chain.

Generally, copolymers of the structure



wherein M₁, M₂ and T are as defined above, and wherein z is an integer of at least 1, are undesirable as viscosity modifier polymers. Solutions of structure V copolymers in oil tend to gel even when the M and T portions have exactly the same composition and molecular weight as structure IV copolymers (with x=z=1). It is believed this poor viscosity modifier performance is due to the inability of a center T segment to sterically stabilize against association.

The M segments of the copolymers of this invention comprise the 1,4-addition product of butadiene which has been hydrogenated, but can also comprise at least one other hydrogenated diolefin monomer, provided the 1,4-polybutadiene content of said M segment is at least about 30 mole percent and a majority of the methylene sequences are sufficiently long, e.g., contain at least about 13 methylene units. The T segments comprise a mixture of hydrogenated butadiene in the 1,2-configuration and the 1,4-configuration and have a 1,4-polybutadiene content not greater than about 20 mole percent. The T and T₂ segments can contain amounts of hydrogenated 1,4-configuration butadiene monomers,

This Sheet Has Been Replaced

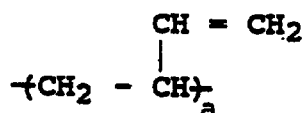


SUBSTITUTE SHEET

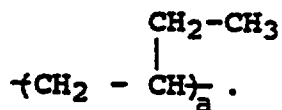
-23-

i.e., 1,4-polybutadiene units, provided the total methylene content of said segments does not exceed about 70 mole percent.

A preferred embodiment, a hydrogenated block or segmented copolymer of 1,4-butadiene and 1,2-butadiene contains at least one crystallizable block or segment and at least one non-crystallizable block or segment. Such block or segment copolymers may be represented by formula IV described hereinbefore, i.e., $T_1-(M_1-T_2)_x-M_2-T_3$ wherein M_1 , M_2 , T_1 , T_2 , T_3 and x are as defined hereinbefore. Preferably, M_1 and M_2 are comprised predominantly or solely of methylene units derived from the polymerized 1,4-butadiene which has subsequently been hydrogenated. T_1 , T_2 and T_3 contain adequate substituted methylenes to render the segments of low crystallinity and may generally be derived, from 1,2-polymerized butadiene which has been hydrogenated. In forming a block copolymer of the structure $T_1 - M_2 - T_3$, butadiene is first polymerized to form 1,2-butadiene monomer units, to form a precursor copolymer T_1' segment containing a recurring structure represented by the formula



wherein a is a number of at least 1. Upon hydrogenation this structure becomes



Upon complete or substantially complete polymerization by 1,2-addition, butadiene monomer is reacted with the "living" 1,2-butadiene segment. The

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-24-

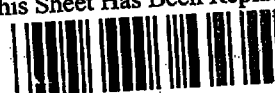
butadiene is polymerized via 1,4-addition (generally there may be some fraction of 1,2-butadiene addition, although this may be kept to a minimum by appropriate reaction conditions), to form a precursor copolymer segment M' containing a recurring structure represented by the formula $\text{-(CH}_2\text{ - CH = CH - CH}_2\text{)}_{a'}$

wherein a' is a number of at least 1. Upon hydrogenation this structure becomes $\text{(CH}_2\text{ - CH}_2\text{ - CH}_2\text{ - CH}_2\text{)}_{a'}$.

Upon completion or substantial completion of polymerization to by 1,4-addition, the 1,2-addition reaction is resumed with the precursor block copolymer $T_1' - M_2' -$, with M_2' being the "living" butadiene block. The 1,2-addition polymerization is continued to form precursor copolymer segment T_3' containing the same recurring structure as precursor copolymer segment T_1' . The precursor copolymer containing segments $T_1' - M_2' - T_3'$ is then hydrogenated to form hydrogenated copolymer of structure $T_1 - M_2 - T_3$.

The present invention relates to novel segmented hydrogenated copolymers of butadiene wherein the copolymer's chain contains at least one crystallizable segment rich in methylene units and at least one low crystallinity segment relatively rich in substituted methylene units, wherein the low crystallinity copolymer segment is characterized in the unoriented bulk state after at least about 48 hours annealing at 23°C by a degree of crystallinity of less than about 0.2% at 23°C, and wherein the copolymer's chain is intramolecularly heterogeneous. The crystallizable segments comprise an average of from about 20 to 90 weight percent, preferably from about 25 to 85 weight percent, and more preferably from about 30 to about 80

This Sheet Has Been Replaced



-25-

weight percent of the total copolymer chain, and contain an average 1,4-polybutadiene content which is at least about 20 mole percent, preferably at least about 30 weight percent. The low crystallinity copolymer segments comprise an average of from about 80 to 10 weight percent, preferably from about 75 to 15 weight percent, and more preferably from about 70 to 20 weight percent of the total copolymer chain, and have a 1,4-polybutadiene content not greater than about 20 mole percent. The copolymers in accordance with the present invention comprise intramolecularly heterogeneous chains, with substantially each chain containing both crystallizable and low crystallinity segments.

The hydrogenated copolymers of the instant invention have weight-average molecular weights ($\overline{M}_w$) as low as about 2,000. The preferred minimum is about 10,000. The more preferred minimum is about 20,000. The maximum weight-average molecular weight can be as high as 2,000,000. The preferred maximum is about 500,000. The more preferred maximum is about 250,000. The M segments have a $\overline{M}_w$ of from about 1,000 to about 1,000,000, preferably from about 10,000 to about 2,000,000, and more preferably about 20,000 to about 100,000. The T segments have a $\overline{M}_w$ of from about 1,000 to about 1,000,000, preferably about 5,000 to about 200,000, and more preferably from about 10,000 to about 100,000. The weight average molecular weights are determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) and light scattering as discussed above.

The copolymers of the instant invention have a molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of about 2.0 or less, preferably about 1.9 or less, and more preferably

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-26-

about 1.8 or less, as determined by SEC as discussed in G. Ver Strate, C. Cozewith, S. Ju, in *Macromolecules*, 21, 3360, 1988.

5 It is believed the novel copolymer's improved function as viscosity modifiers can be at least partially attributed to the ability of a controlled portion of the copolymer's molecules to crystallize in oleaginous compositions such as lubricating oils at temperatures above the cloud point of the lubricating
10 oil. This occurs both inter- and intra-molecularly.

Typical lubricating oil contains paraffinic and isoparaffinic waxy components which are capable of crystallizing. As the lubricating oil is cooled from high temperatures (above T_C), these waxy components
15 begin to crystallize. When the crystals become large they scatter light and make the oil turbid (the cloud point, T_C). Below the cloud point, waxes in the oil can co-crystallize with the crystallizable viscosity modifier crystallizable segments, effectively
20 crosslinking the viscosity modifier polymer molecules, resulting in high "effective" polymer molecular weights, or causing "gelation" of the oil. This is observed by the appearance of a yield stress upon shearing. Such effectively high molecular weights are
25 undesirable, as they increase the oil viscosity at low temperatures making it difficult for the oil to be pumped or poured.

The associated copolymer molecules of this invention are believed to have a smaller effective
30 hydrodynamic volume per molecule than in their unassociated state, which lowers the relative viscosity of the lubricating oil solution thereof and provides low formulated oil viscosities at low temperatures. It

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-27-

is believed the copolymer's characteristics of exhibiting a higher polymer association temperature than the oil's cloud point minimizes interaction with the wax in the oil and accordingly decreases the tendency of oils to undergo gelation. Also, only a portion of these copolymer molecules is crystallizable under the use conditions. The non-crystallizable portion is believed to act as a steric barrier to help prevent excessive intermolecular association. The controlled segmented nature of the polymers is essential to their performance.

If the polymer has already associated above the cloud point temperature, the polymer and wax have little opportunity to interact. Furthermore, if the polymer contains segments which are low enough in methylene to completely avoid crystallization and are properly located along the contour, these will act as steric blocks to wax or excessive polymer/polymer interaction. Thus, two polymer characteristics are needed: crystallization above the wax appearance temperature and a segmented structure to stabilize agglomeration before gels form.

The copolymers of the present invention are preferably prepared by anionic polymerization. This method of polymerization offers certain unique advantages which makes it extremely useful in the synthesis of the polymers of the present invention. In particular, by the use of anionic polymerization, it is possible to obtain polymers having a narrow molecular weight distribution, to obtain tapered or block polymers, and to control the structure of the polymers derived from conjugated dienes.

This Sheet Has Been Replaced



-28-

Unlike free-radical polymerization reactions, anionic polymerizations can be performed where there is no facile chemical termination step. Of course, termination reactions do occur, but under carefully selected conditions with the monomers of the present invention, using inert solvents and highly pure reactants, the end groups have indefinite lifetimes. The non-terminated chains derived from anionic homopolymerization can be used for the synthesis of block polymers by sequential addition of different monomers as described hereinbefore. Thus anionic polymerization offers flexibility in allowing either block or tapered polymers to be readily produced. As mentioned hereinbefore polymers with narrow molecular weight distribution having better shear stability than those with broader distributions can be produced. Shear stability is a desirable property in polymers used as viscosity index improvers.

Anionic polymerization generally offers a wider latitude of techniques for producing varied structures of conjugated diolefin polymers. With butadiene monomer, 1,4- and 1,2-addition can be regulated by the appropriate combination of reaction conditions, including catalyst, solvent type, and temperature. Hydrogenated precursor copolymers containing butadiene units predominantly in the 1,4-configuration are much more effective in increasing the V.I. than hydrogenated precursor copolymers containing butadiene units predominantly in the 1,2-configuration.

The polymers of the present invention can be prepared with known metallic and organometallic catalysts such as lithium metal or sodium metal and organo-lithium or organosodium catalysts. Preferred lithium compounds are compounds containing two lithium

This Sheet Has Been Replaced



Academic Press, Inc. (1980). Suitable organo-lithium catalysts may be represented by the formula R^2Li wherein R^2 is a C_3 to C_{30} , and preferably C_3 to C_{10} alkyl, aralkyl, or cycloalkyl group. Specific examples of suitable catalysts include n-propyllithium, isopropyllithium, n-butyllithium, tertiarybutyllithium, n-decyl-
10 lithium, etc. Particularly preferred are the butyllithiums, i.e., normal-, sec-, iso-, and tertiary-
15 butyllithiums.

An inert diluent, in which the catalyst is soluble, may be employed. By "inert" it is meant that
20 the diluent does not react, although the nature of the solvent may affect the relative amount of 1,2- and 1,4-configuration that is obtained. The inert diluent will generally be a hydrocarbon free of olefinic unsaturation containing from 3 to 16 carbon atoms.
25 Suitable inert diluents include aliphatics, such as n-pentane, n-hexane, isooctane, n-nonane, etc.; alicyclics, such as cyclopentane, cyclohexane, cycloheptane, etc., aromatics such as benzene, toluene, xylene, chlorobenzene, etc. The amount of diluent
30 employed in the preparation is not critical, except that sufficient amounts should be used to solubilize the amount of organolithium catalyst used. Generally, 0.5 to 200, preferably 1 to 50 liters of the diluent per gram mole of organo-lithium catalyst are employed
35 during the preparation of the polymer.

SUBSTITUTE SHEET



-30-

The amount of catalyst employed primarily depends upon the degree of polymerization desired. The term "degree of polymerization," as employed herein, means the total number of monomeric units present in the polymer. Ordinarily, each mole of organo-lithium catalyst will generate a mole of polymer. Thus, "degree of polymerization" may be conveniently defined by the generalization:

Degree of polymerization = $\frac{\text{total moles of monomer}}{\text{moles of organo-lithium catalyst}}$

Since to obtain the desired molecular weights, the average number of monomeric units in the polymer will generally be from about 500 to about 10,000. About 0.0001 to 0.002 mole of organolithium catalyst per mole of monomer will ordinarily be utilized.

The polymerization reaction generally takes place at about -50° to about 150°C, and preferably at 20° to 60°C. Reaction times as short as 1 minute or as long as 75 hours may be employed. Preferably, the polymerization reaction is carried out for from 4 minutes to 24 hours. Reaction pressure is not critical; pressures may range from atmospheric to super-atmospheric. Preferably for economy and ease of handling, atmospheric pressure is utilized.

In one embodiment the monomers are added sequentially whereby block or segment copolymers may be obtained. For example in the preparation of a copolymer of structure III, i.e., T - M, one of the monomers, e.g., butadiene, is polymerized in the presence of the catalyst via 1,4-addition for a period of time, e.g., 2 hours, to form a unhydrogenated precursor copolymer segment M' containing at least

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-31-

about 65 weight percent butadiene in the 1,4-configuration. Then the conditions of polymerization are changed for polymerization to take place through 1,2-addition. The comonomer forms 1,2-butadiene units resulting in unhydrogenated precursor segment T'. The segmented copolymer is then hydrogenated to form methylene rich segment M, corresponding to a 1,4-polybutadiene content of at least about 20 weight percent, and substituted methylene rich segment T having a methylene content corresponding to 1,4-polybutadiene of less than about 20 mole percent.

A hydrogenated copolymer having structure IV, i.e., $T_1-M_2-T_3$, can be prepared by first polymerizing butadiene by 1,2-addition, to form unhydrogenated precursor segment T_1' containing predominantly 1,2-butadiene units; the reaction conditions are changed and the butadiene monomer is polymerized (in the presence of T_1') via 1,4-addition mechanism to form unhydrogenated precursor segment M_2' containing at least about 20 mole percent of 1,4-configuration butadiene; and then the reaction conditions changed to polymerize the butadiene via 1,2-addition to form unhydrogenated precursor segment T_3' containing predominantly 1,2-butadiene. The segmented copolymer $T_1'-M_2'-T_3'$ is then hydrogenated to form the $T_1-M_2-T_3$ structure.

In the foregoing discussion concerning the preparation of copolymers of structures M - T and $T_1 - M_2 - T_3$ it is to be understood that the M segment need not contain, and usually does not contain, only methylene units derived from the hydrogenation of 1,4-addition butadiene. It may also contain some substituted methylene units derived from the hydrogenation of the 1,2-addition butadiene so long as

This Sheet Has Been Replaced



-32-

those substituted methylene units do not exceed about 80 mole percent of the total units. Likewise, segments T, T₁ and T₃ may contain, and usually do contain, methylene units derived from the hydrogenation of 1,4-addition butadiene, so long as the total methylene units present in T, T₁ and T₃ do not correspond to a 1,4-polybutadiene content exceeding 20 mole percent.

An alternate and preferred embodiment of the present invention is one wherein the copolymer is in a star polymer form, i.e., a star block copolymer. A living block copolymer having monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products of the polymerization of butadiene is formed as recited above. The copolymer has the above structures of T-M and T₁-M₂-T₃. When the copolymer reaches a desired molecular weight a polyalkenyl coupling agent is introduced. The polyalkenyl coupling agent acts as a nucleus of the star. The living polymers react at one end with the polyalkenyl coupling agent. The living polymer is then deactivated or killed in a known manner. Each arm of the star is thereby attached at one end to the nucleus with the opposite end preferably being a "T" segment. That is, the free ends of the arms of the star are preferably rich in substituted methylene units making them amorphous.

Each arm of the star preferably has the character of the straight chain copolymer from which it forms. For the purposes of the present invention the term block copolymer will therefore include star copolymers containing arms which have blocks consistent with the straight chain block copolymers recited above. Preferred molecular weights for star polymers are higher than their linear counterparts.

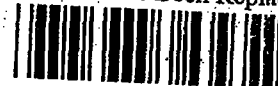


-32-

those substituted methylene units do not exceed about 80 mole percent of the total units. Likewise, segments T, T₁ and T₃ may contain, and usually do contain, methylene units derived from the hydrogenation of 1,4-addition butadiene, so long as the total methylene units present in T, T₁ and T₃ do not correspond to a 1,4-polybutadiene content exceeding 20 mole percent.

An alternate and preferred embodiment of the present invention is one wherein the copolymer is in a star polymer form, i.e., a star block copolymer. A living block copolymer having monomeric units derived from 1,4-butadiene and 1,2-butadiene addition products of the polymerization of butadiene is formed as recited above. The copolymer has the above structures of T-M and T₁-M₂-T₃. When the copolymer reaches a desired molecular weight a polyalkenyl coupling agent is introduced. The polyalkenyl coupling agent acts as a nucleus of the star. The living polymers react at one end with the polyalkenyl coupling agent. The living polymer is then deactivated or killed in a known manner. Each arm of the star is thereby attached at one end to the nucleus with the opposite end preferably being a "T" segment. That is, the free ends of the arms of the star are preferably rich in substituted methylene units making them amorphous.

Each arm of the star preferably has the character of the straight chain copolymer from which it forms. For the purposes of the present invention the term block copolymer will therefore include star copolymers containing arms which have blocks consistent with the straight chain block copolymers recited above. Preferred molecular weights for star polymers are higher than their linear counterparts.



-33-

Apart from the specific and improved character of the block copolymer structure of the arms, the star polymers of the present invention are made in accordance with procedures disclosed in patents such as U. S. Patent No. 4,358,565 and U. S. Patent No. 4,620,048. The improvement of the star copolymer of the present invention being that it is a copolymer having arms wherein there are sharp blocks characterized by their amorphous and crystalline properties. The configurations having methylene rich groups at the arms of the stars near the star center are useful in lubricating oils which contain paraffin and isoparaffinic waxy components capable of crystallizing to prevent crystalline gelling.

More particularly, the star polymers of the present invention are made by forming block copolymers as recited above. The block copolymers have a structure as presented in formulas III, and IV with the structure of IV being most preferred. The living block copolymer is first prepared by copolymerizing blocks of butadiene and isoprene as recited above.

In a preferred method the living block copolymers produced are reacted with a polyalkenyl coupling agent such as a polyvinyl compound, or halosilane compounds such as SiCl_4 . Such polyalkenyl coupling agents capable of forming star-shaped polymer are known and indicated to be disclosed in polymers such as in U. S. Patent No. 3,985,830.

The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e., the agent should only be added after substantially all of the

This Sheet Has Been Replaced



-35-

addition of a second compound which reacts with the carbon-ionic end group. Examples of suitable de-activators include compounds with one or more active hydrogen such as water, alcohol, such as methanol, ethanol, isopropanol, 2-ethylhexanol, or carboxylic acids such as acetic acid, compounds with one active halogen atom, such as chlorine atoms (benzyl chloride or fluoromethane), compounds with one ester group and carbon dioxide. If not deactivated in this way, the living star-shaped polymers will be killed by the hydrogenation step. Before being killed, the living star-shaped polymers may be reacted with further amounts of monomers, such as the same or different dienes, or functional monomers.

The molecular weights of the star-shaped polymer to be hydrogenated may vary between relatively wide limits. However, they are typically between molecular weights from about 25,000 to 1,500,000, and preferably from 100,000 to 500,000. The molecular weights are weight average molecular weights determined by gel permeation chromatography.

The hydrogenation of the polymers of the present invention is carried out using conventional hydrogenation procedures. The polymer is diluted with an inert solvent, such as those previously mentioned, or in the original polymerization medium, and the polymer solution and hydrogenation catalyst are added to a high pressure autoclave. The autoclave is pressured with hydrogen to about 100 to 3,000 p.s.i.g., and then heated to 50° to 220°C, (preferably 75° to 150°C), for about 0.1 to 24, preferably 1 to 24 hours (preferably 2 to 10 hours), while mixing. The reactor is then depressurized, the catalyst removed by

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-36-

filtering, and the hydrogenated polymer recovered from the solvent by conventional stripping procedures.

The hydrogenation catalyst will generally be used in an amount of 0.1 to 20 weight percent based upon the weight of the polymer to be hydrogenated. The specific amount of catalyst employed depends somewhat upon the specific catalyst used. Any material functioning as an olefin hydrogenation catalyst can be used; suitable catalysts include Raney nickel, platinum oxide, platinum on alumina, palladium or charcoal, copper chromate, nickel supported on kieselguhr, molybdenum sulfide, and the like. The best hydrogenation results were obtained with Raney nickel, in large excess, at high temperatures and pressure. Co or Ni carboxylates reduced with aluminum alkyls can also be used.

Hydrogenation is carried out to remove the olefinic unsaturation present in the precursor copolymer. Hydrogenation may be complete or substantially complete. By complete hydrogenation is meant that all of the olefinic bonds are saturated. By substantially complete hydrogenation is meant that substantially all of the olefinic unsaturation is saturated. By substantially all olefinic unsaturation is meant at least about 80%, preferably at least about 90% of the olefinic unsaturation and most preferably greater than 98%.

Another embodiment of the present invention is a tapered block or segmented copolymer of the hydrogenated 1,2- and 1,4-butadiene. A tapered block or segmented copolymer according to this invention is a copolymer obtained by anionically copolymerizing in hydrocarbon solution in, for example, a batch reactor a mixture containing butadiene monomer to form a

This Sheet Has Been Replaced



-37-

precursor copolymer having at least 75 weight percent 1,4-configuration of the 1,4-butadiene and then hydrogenating said precursor copolymer.

5 The anionic polymerization and subsequent hydrogenation conditions used in the preparation of the tapered segmented or block copolymer are substantially the same as those described hereinbefore. The weight-average molecular weights of these tapered segmented or block hydrogenated copolymers are generally the same as
10 those described above.

The weight percent of the butadiene present in the reaction mixture is that which is effective to form a tapered segmented or block copolymer having at least one crystallizable segment and at least one low
15 crystallinity segment. Generally this amount of butadiene is from about 20 to about 90 weight percent. Additionally, the amount of the 1,4-configuration butadiene present in the precursor copolymer must be an amount which is effective to form a crystallizable
20 segment upon hydrogenation of the precursor copolymer. Generally, this amount is at least about 20 mole percent.

The polymers can be recovered by procedures well known in the art. For example, polar materials, such
25 as water or C₁ to C₅ alkanols can be added to inactivate the catalyst. Preferably, the reaction is terminated by dropping the reaction system into 2 to 10 volumes of methanol containing about 0.1 weight percent antioxidant. After termination of the reaction, the
30 hydrocarbon solution is washed with water or dilute mineral acid. Alternatively, the active polymer solution can be treated with hydrated clays, such as natural Attapulgu clay, which functions to both

This Sheet Has Been Replaced



-38-

inactivate the catalyst and to chemically absorb the lithium component. The polymer may be recovered by filtering the resultant polymer solution, drying if necessary, and stripping of remaining inert diluent at elevated temperatures (e.g., 70° to 120°C) and reduced pressures (e.g., 0.1 to 100 mm. Hg). For the isolation of higher molecular weight polymers steam stripping or precipitation with anti-solvents is preferred.

By controlling the ratio of 1,4- to 1,2-butadiene in the anionic polymerization it is possible to obtain an effective wide range of methylene to substituted methylene ratio in the hydrogenated product.

When the polymerization of the dienes has been completed, the copolymer thus obtained can be hydrogenated either immediately or after recovery to obtain the desired hydrogenated copolymers according to the invention.

The present invention includes compositions comprising an oleaginous material such as lubricating oil and at least one hydrogenated block copolymer as described. There can be a minor amount, e.g. 0.01 up to 50 weight percent, preferably 0.05 to 25 weight percent, based on the weight of the total composition, of the hydrogenated copolymer produced in accordance with this invention can be incorporated into a major amount of an oleaginous material, such as a lubricating oil or hydrocarbon fuel, depending upon whether one is forming finished products or additive concentrates. When used in lubricating oil compositions, e.g. automotive or diesel crankcase lubricating oil, copolymer concentrations are usually within the range of about 0.01 to 10 weight percent, of the total composition. The copolymers of the invention may be



-39-

utilized in a concentrate form, e.g., from about 5 weight percent up to about 50 weight percent, preferably 7 to 25 weight percent oil, e.g., mineral lubricating oil, for ease of handling, and may be prepared in this form by carrying out the reaction of the invention in oil as previously discussed. The lubricating oils to which the products of this invention can be added include not only hydrocarbon oil derived from petroleum, but also include synthetic lubricating oils such as esters of dibasic acids; complex esters made by esterifications of monobasic acids, polyglycols, dibasic acids and alcohols; polyolefin oils, etc. The hydrogenated copolymers of the present invention are particularly useful as fuel and lubricating oil additives, particularly as Viscosity Index improver lubricating oil additives.

The hydrogenated copolymers of the instant invention are oil-soluble, dissolvable in oil with the aid of a suitable solvent, or are stably dispersible therein. The terms oil-soluble, dissolvable in oil, or stably dispersible in oil as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the additives for instance, are soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular copolymer hereof, if desired.

The copolymers are particularly useful in lubricating oil compositions, which employ a base oil in which these copolymers are dissolved or dispersed.

This Sheet Has Been Replaced



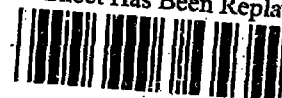
-40-

Base oils suitable for use in preparing the lubricating compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additives of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention.

The above oil compositions may optionally contain other conventional additives, pour point depressants, antiwear agents, antioxidants, other viscosity-index improvers, dispersants, corrosion inhibitors, anti-foaming agents, detergents, rust inhibitors, friction modifiers, and the like.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-41-

such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of about 66 to about 316°C. Neutralization of the phospho-sulfurized hydrocarbon may be effected in the manner taught in U. S. Patent No. 1,969,324.

Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, e.g., calcium nonylphenol sulfide, barium toctylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Other oxidation inhibitors or antioxidants useful in this invention comprise oil-soluble copper compounds. The copper may be blended into the oil as any suitable oil-soluble copper compound. By oil soluble it is meant that the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates. Alternatively, the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples of same thus include C₁₀ to C₁₈ fatty acids, such as stearic or palmitic acid, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weights of from about 200 to 500, or synthetic carboxylic acids, are preferred,

This Sheet Has Been Replaced



SUBSTITUTE SHEET

-42-

because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil-soluble copper dithiocarbamates of the general formula $(RR,NCSS)_nCu$ (where n is 1 or 2 and R and R , are the same or different hydrocarbyl radicals containing from 1 to 18, and preferably 2 to 12, carbon atoms, and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R , groups are alkyl groups of from 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n -propyl, i -propyl, n -butyl, i -butyl, sec -butyl, amyl, n -hexyl, i -hexyl, n -heptyl, n -octyl, decyl, dodecyl, octadecyl, 2-ethyl hexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e., R and R ,) will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

Exemplary of useful copper compounds are copper CuI and/or $CuII$ salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) polyalkylene succinimides (having polymer groups of M_n of 700 to 5,000) derived from polyalkylene-polyamines, which have at least one free carboxylic acid group, with (b) a reactive metal compound. Suitable reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, borates, and carbonates or basic copper carbonate.

Examples of these metal salts are Cu salts of polyisobutenyl succinic anhydride, and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu^{+2} . The



-43-

preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a molecular weight greater than about 700. The alkenyl group desirably has a $\overline{Mn}$ from about 900 to 1,400, and up to 2,500, with a $\overline{Mn}$ of about 950 being most preferred. Especially preferred is polyisobutylene succinic anhydride or acid. These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70 and about 200°C. Temperatures of 110°C to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

The copper antioxidants (e.g., Cu-polyisobutenyl succinic anhydride, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from about 50 to 500 ppm by weight of the metal, in the final lubricating or fuel composition.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U. S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U. S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U. S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U. S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U. S. Patent No. 3,778,375 which discloses reaction products of a

This Sheet Has Been Replaced



-44-

phosphonate with an oleamide; U. S. Patent No. 3,852,205 which discloses S-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; U. S. Patent No. 3,879,306
5 which discloses N(hydroxyalkyl)alkenyl-succinamic acids or succinimides; U. S. Patent No. 3,932,290 which discloses reaction products of di- (lower alkyl) phosphites and epoxides; and U. S. Patent No. 4,028,258
10 which discloses the alkylene oxide adduct of phospho-sulfurized N-(hydroxyalkyl) alkenyl succinimides. The disclosures of the above references are herein incorporated by reference. The most preferred friction
modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides
15 and thiobis-alkanols such as described in U. S. Patent No. 4,344,853.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation
20 or deposition on metal parts. Suitable dispersants include high molecular weight polyalkenyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

25 Pour point depressants, otherwise known as lube oil flow improvers, lower the temperature at which the fluid will flow or can be poured. Such additives are well known. Typically of those additives which usefully optimize the low temperature fluidity of the
30 fluid are C₈-C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, e.g., silicone oil and polydimethyl siloxane.

This Sheet Has Been Replaced



-45-

Anti-wear agents, as their name implies, reduce wear of metal parts. Representatives of conventional antiwear agents are zinc dialkyldithio- phosphate and zinc diaryldithiosphate.

5 Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz, overbased)
10 metal sales, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents. Representative examples of such materials, and their methods of preparation, are found in co-pending Serial No. 754,001, filed July 11, 1985,
15 the disclosure of which is hereby incorporated by reference.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be
20 further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts
25 of such additives are illustrated as follows:

This Sheet Has Been Replaced



-46-

	Additive	Wt. % (Broad)	Wt. % (Preferred)
5	Viscosity Modifier	.01-12	.01-4
	Corrosion Inhibitor	0.01-5	.01-1.5
	Oxidation Inhibitor	0.01-5	.01-1.5
10	Dispersant	0.1-20	0.1-8
	Pour Point Depressant	0.01-5	.01-1.5
	Anti-Foaming Agents	0.001-3	.001-0.15
15	Anti-Wear Agents	0.001-5	.001-1.5
	Friction Modifiers	0.01-5	.01-1.5
20	Detergents/Rust Inhibitors	0.01-10	.01-3
	Mineral Oil Base	Balance	Balance

- 25 When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the viscosity index modifying copolymers (in concentrate amounts hereinabove described),
- 30 together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to here in as an additive package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition.
- 35 Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the viscosity index
- 40 improving copolymer additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the products of the

This Sheet Has Been Replaced



-48-

MRV (Mini Rotary Viscometer), using a technique described in ASTM-D3829, measures viscosity in centipoise and yield stress in Pascals. MRV is determined at -25°C.

5 CCS (Cold Cranking Simulator), using a technique in ASTM-D2602, a high shear viscosity measurement in centipoises. This test is related to a lubricating oil's resistance to cold engine starting.

10 TP1 cycle MRV--Determined by ASTM D4684. This is essentially the same as the ASTM MRV noted above, except a slow cooling cycle is used. The cycle is defined in SAE Paper No. 850443, K. O. Henderson et al.

15 The copolymer of the present invention, when used to formulate lubricating oils, will lower the viscosity measured using the Cold Cranking Simulator Test. At the same time, low TP-1 cycle MRV is maintained or lowered. The thickening efficiency (TE) is improved and the lube oil has high viscosity at high temperatures and low viscosity at low temperatures.

20 The following Example further illustrates the present invention. Unless otherwise stated, all of said weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package,
25 or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

EXAMPLE

30 Thickening efficiency (T.E.) is defined as the ratio of the weight percent of a polyisobutylene (sold

This Sheet Has Been Replaced



-49-

as an oil solution by Exxon Chemical Company as Paratone[®] N), having a Staudinger molecular weight of 20,000, required to thicken a solvent-extracted neutral mineral lubricating oil, having a viscosity of 150 SUS at 37.8°C, a viscosity index of 105 and an ASTM pour point of O.F. (Solvent 150 Neutral) to a viscosity of 12.4 centistokes at 98.9°C to the weight percent of a test copolymer required to thicken the same oil to the same viscosity at the same temperature. For linear polymers of a given methylene content, the thickening efficiency is approximately proportional to the 0.75 power of the weight-average molecular weight.

In this Example a polymer having crystallizable and non-crystallizable segments is prepared from butadiene by controlling the relative proportions of 1,2 butadiene and 1,4 butadiene, using a high vacuum polymerization techniques. The experimental procedure is of the type described in M. Morton, L. J. Fetters, Rubber Chem. Tech., 48, 359 (1975).

500 grams of cyclohexane is charged to a 2 liter reaction flask. To this is added 0.5 millimeters of dilithium isoprene oligomer initiator (DILI) sold by Lithcoa and 54 grams of butadiene. The mixture is allowed to react to form a predominantly (1,4 poly butadiene) at 24°C for about 24 hours.

Dipiperidylethane (DPE) from Reilly Tire and Chemical Co. or Aldrich is then added as a modifier at 2:1 mole ratio based on Li, as discussed in A. Halasa, D. Schulz, D. Tate, V. Mochel, Adv. Organometallic Chem., 18, 55, (1980). An additional 54 grams of butadiene is added and the polymerization proceeds at about 0°C for 48 hours to form a block of predominantly 1,2 poly butadiene and at each end of the (1,4 poly-

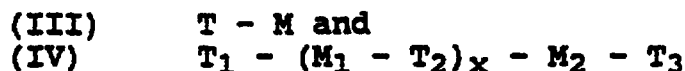


-51-

CLAIMS:

1. A hydrogenated polybutadiene block copolymer comprising monomeric units of 1,4-butadiene and 1,2-butadiene polymerization product, the copolymer being
5 hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to 1,4-polybutadiene content of at least about 20 mole percent, and at least one low
10 crystallinity segment comprised of methylene units and substituted methylene units and having an average 1,4-polybutadiene content less than about 20 mole percent.

2. The hydrogenated copolymer as recited in claim 1 containing chain segment sequence represented
15 by at least one of the structures:



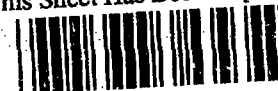
wherein x is a number of from 0 to 3, M comprises said
20 crystallizable segment, T comprises said low crystallinity segment, M_1 and M_2 are the same or different and each comprises said crystallizable segment, and T_1 , T_2 and T_3 are the same or different
25 and each comprises said low crystallinity segment.

3. The hydrogenated copolymer as recited in claim 2 wherein said chain segment sequence is represented by (III).

4. The hydrogenated copolymer as recited in
30 claim 2 wherein said chain segment sequence is represented by (IV).

5. The hydrogenated copolymer as recited in claim 4 wherein x is zero.

This Sheet Has Been Replaced



SUBSTITUTE SHEET



-53-

average methylene content of less than about 70 mole percent.

14. The hydrogenated copolymer as recited in claim 1 wherein the crystallizable segment has a number average molecular weight of at least 500.

15. The hydrogenated copolymer as recited in claim 1 wherein the copolymer is a star block copolymer.

16. The hydrogenated copolymer as recited in claim 15 wherein the star block copolymer has from 4 to 25 arms.

17. The hydrogenated copolymer as recited in claim 16 wherein the star block copolymer has from 5 to 15 arms.

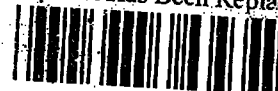
18. The hydrogenated copolymer as recited in claim 15 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

19. A process comprising the steps of:

polymerizing a precursor polybutadiene block copolymer comprising at least one crystallizable segment comprising 1,4-butadiene and at least one comonomer low crystallinity segment comprising comonomer units 1,2-butadiene, the copolymer comprising at least 10 percent by weight of the crystallizable segments,

substantially hydrogenating the precursor block copolymer to form a hydrogenated block copolymer and comprising at least 10 percent by weight of at

This Sheet Has Been Replaced





-54-

least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of at least about 20 mole percent, and at least one low
5 crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene corresponding to a 1,4-polybutadiene content of less than about 20 mole percent.

10 20. The process as recited in claim 19 where the butadiene comprises at least 30 mole percent 1,4-butadiene.

21. The process as recited in claim 19 wherein the polymerization is anionic polymerization.

15 22. The process as recited in claim 21 polymerizing a precursor block copolymer further comprising

first controlling the polymerization to form crystallizable segments, and

20 then controlling the polymerization to form low comonomer crystallinity segments comprising at least 70 mole percent of 1,2-butadiene monomeric units.

23. The process as recited in claim 21 polymerizing a precursor block copolymer further comprises

25 first controlling the polymerization to form a comonomer segments comprising at least 70 mole percent of 1,2-butadiene monomeric units;





-55-

then controlling the polymerization to form 1,4-butadiene segments; and

5 then controlling the polymerization to form comonomer segments comprising at least 70 mole percent of 1,2-butadiene monomeric units.

24. The process as recited in claim 23 further comprising the step of introducing a coupling agent after forming the precursor block copolymer to form a star block copolymer.

10 25. The process as recited in claim 24 wherein the star block copolymer has from 4 to 25 arms.

26. The process as recited in claim 25 wherein the star block copolymer has from 5 to 15 arms.

15 27. The process as recited in claim 24 wherein the star block copolymer has a weight average molecular weight of from 100,000 to 500,000.

20 28. A composition comprising (a) oil; and (b) at least one hydrogenated polybutadiene block copolymer comprising monomeric units of 1,4-butadiene and 1,2-butadiene polymerization products, the copolymer being hydrogenated and comprising at least 10 percent by weight of at least one crystallizable segment comprised of methylene units and having an average methylene content corresponding to a 1,4-polybutadiene content of
25 at least about 20 mole percent, and at least one low crystallinity segment comprised of methylene units and substituted methylene units and having an average methylene content less than about 75 mole percent.





-56-

29. The composition as recited in claim 28 wherein said hydrogenated copolymer is comprised of chain segment sequence represented by at least one of the structures:

- 5 (III) T - M and
(IV) $T_1 - (M_1 - T_2)_x - M_2 - T_3$

10 wherein x is a number of from 0 to 3, M comprises said crystallizable segment, T comprises said low crystallinity segment, M_1 and M_2 are the same or different and each comprises said crystallizable segment, and T_1 , T_2 and T_3 are the same or different and each comprises said low crystallinity segment.

15 30. The composition as recited in claim 28 wherein said chain segment sequence is represented by (III).

20 31. The composition as recited in claim 28 wherein said chain segment sequence is represented by (IV).

32. The composition as recited in claim 31 wherein x is zero.

25 33. The composition as recited in of claim 32 wherein said T_1 and T_3 segments are of substantially the same weight average molecular weight.

30 34. The composition as recited in claim 28 wherein the 1,4-butadiene and 1,2-butadiene are present in amounts effective to provide said at least one crystallizable segment and said at least one low crystallinity segment.

This Sheet Has Been Replaced





-60-

57. The process as recited in claim 49 wherein said hydrogenated copolymer has a molecular weight distribution characterized by a ratio of $\overline{Mw}/\overline{Mn}$ of less than 2.

5 58. The process as recited in claim 49 wherein said oil is lubricating oil.

59. The process as recited in claim 58 which is a lubricating oil concentrate.

10 60. The process as recited in claim 58 which is a fully formulated lubricating oil composition.

61. The process as recited in claim 49 wherein said oil is lubricating oil.

15 62. The process as recited in claim 49 wherein the crystallizable segment comprises at least 11 adjacent methylene units in series.

63. The process as recited in claim 62 wherein the low crystallinity segment comprises less than 11 adjacent methylene units in series.

20 64. The process as recited in claim 63 wherein the low crystallinity segment comprises less than 7 adjacent methylene units in series.

65. The process as recited in claim 49 wherein the crystallizable segment has a number average molecular weight of at least 500.

25 66. The process as recited in claim 49 wherein the copolymer is a star block copolymer.

This Sheet Has Been Replaced

