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3,244,773

ADDITION OF TRANS-POLYBUTADIENE TO PREVENT COLD FLOW IN CIS-POLYBUTADIENE

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This invention relates to a method for preventing or substantially reducing the tendency of cis-polybutadiene to cold flow. In one aspect, it relates to a novel composition containing cis-polybutadiene and trans-polybutadiene, in which the tendency of cis-polybutadiene to cold flow is substantially reduced.

In recent years, a great deal of research work has been conducted in the field of olefin polymerization. Great advantages have been recently made in this field as the result of the discovery of new catalyst systems. These catalyst systems are often described as being "stereospecific" since they are capable of polymerizing monomers, particularly conjugated dienes, to a certain geometric configuration. One of the products which has attracted widespread attention because of its superior properties is a polybutadiene containing a high percentage, e.g., at least 85 percent, of cis 1,4-addition. The physical properties of this high cis-polybutadiene are of such a nature that the polymer is particularly suitable for the fabrication of heavy duty tires and other articles for which conventional synthetic rubbers have heretofore been comparatively unsatisfactory. However, in the processing of high cis-polybutadiene, particularly in packaging, shipping and storage, a certain amount of difficulty has been encountered because of the tendency of the polymer to cold flow when in the unvulcanized state. For example, if cracks or punctures develop in the package used in storing the polymer, polymer will flow from the package with a resulting loss or contamination and sticking together of stacked packages.

It is an object of this invention, therefore, to provide a method for eliminating or substantially reducing the tendency of cis-polybutadiene to cold flow when in the unvulcanized state.

Another object of the invention is to provide a novel composition which contains cis-polybutadiene and a minor amount of a trans-polybutadiene which prevents or substantially reduces cold flow.

Other and further objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

The present invention resides in the discovery that the tendency of cis-polybutadiene to cold flow can be reduced or substantially eliminated by blending the material with a trans-polybutadiene. Broadly speaking, the composition of this invention comprises (1) a major amount of a cis-polybutadiene containing at least 85 percent cis 1,4-addition, and (2) a minor amount of a trans-polybutadiene containing at least 70 percent trans 1,4-addition. Usually, the composition of this invention is prepared by blending with a cis-polybutadiene from 0.1 to 10.0 parts by weight of a trans-polybutadiene per 100 parts by weight of the mixture of cis-polybutadiene and trans-polybutadiene. The blending operation is usually conducted at an elevated temperature, e.g., at a temperature in the range of 175 to 350° F. It is preferred to carry out the blending at a temperature in the range of 275 to 325° F. because the

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maximum reduction in cold flow is obtained when operating in this temperature range.

Any suitable method which will give a homogeneous blend can be used in blending the cis-polybutadiene with the trans-polybutadiene. A convenient method is to blend the materials on a roll mill, in a Banbury mixer, or similar kneading device. The mixing operation is conducted at an elevated temperature as specified hereinabove. The mixing operation is continued for a period of time sufficient to obtain a homogeneous composition, e.g., for a period in the range of about 30 seconds to 10 minutes or longer. In another method for blending the materials, solutions of the polymers in the hydrocarbon solvent are blended and the products are recovered by conventional means, such as by steam stripping, coagulation in an alcohol, such as isopropyl alcohol, or the like. After the blending operation is completed, the polymer composition can then be packaged and stored or transferred for utilization elsewhere. The composition can be blended, compounded, fabricated and cured according to procedures which are well known in the rubber art.

The trans-polybutadiene used in the present composition contains a high percentage, e.g., at least 70 percent, of trans 1,4-addition. A trans-polybutadiene suitable for use contains from about 70 to 95 percent and higher of trans 1,4-addition, the remainder of the polymer being formed by 1,2-addition and cis 1,4-addition. The amount of unsaturation other than trans-unsaturation present in the polymers appears to be immaterial. It is to be understood that the present invention is, in general, applicable to any synthetic polybutadiene in which the above-mentioned percentage of the polymer is formed by trans 1,4-addition of the monomer.

The present invention is applicable to blends of cis-polybutadiene and trans-polybutadiene regardless of the method employed in preparing the polymers. One method that can be advantageously utilized in preparing the trans-polybutadiene comprises the step of polymerizing 1,3-butadiene in the presence of a catalyst composition comprising (a) a complex aluminum hydride of an alkali metal, such as lithium aluminum hydride, and (b) titanium tetraiodide. The amount of the hydride used in the catalyst composition is usually in the range of 0.5 to 6 moles per mole of titanium tetraiodide with a preferred mole ratio being from 1.3 to 3.0. The polymerization is generally carried out at a temperature in the range of 10° C. to 80° C. in the presence of an inert hydrocarbon diluent. Diluents suitable for use include aromatics, such as benzene and toluene, and paraffins, such as normal pentane and isooctane. It is frequently preferred to charge the complex aluminum hydride to the reactor as a solution in a dialkyl ether, such as diethyl ether. This method of preparing trans-polybutadiene is described in detail by R. P. Zelinski and D. R. Smith in U.S. Patent No. 3,050,513.

The present invention is generally applicable to polybutadienes containing a high percentage of cis 1,4-addition. It is usually preferred that this cis-polybutadiene contain at least 85 percent, cis 1,4-addition, e.g., 85 to 98 percent and higher. The cis-polybutadiene can be prepared by polymerizing 1,3-butadiene with any one of a large number of different stereo-specific catalyst systems. It is usually preferred to employ a catalyst which is selected from the group consisting of (1) a catalyst comprising an organometal compound having the formula R_mM , where-

in R is an alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkyl-cycloalkyl, cycloalkylalkyl, arylcycloalkyl or cycloalkyl-aryl radical, M is aluminum, mercury, zinc, beryllium, cadmium, magnesium, sodium or potassium, and m is equal to the valence of the metal M, and titanium tetraiodide, (2) a catalyst comprising an organometal compound having the formula R_nM' , wherein R is an organo radical as defined above, M' is aluminum, magnesium, lead, sodium or potassium, and n is equal to the valence of the metal M' , titanium tetrachloride and titanium tetraiodide, (3) a catalyst comprising an organometal compound having the formula R_aM'' , wherein R is an organo radical as defined above, M'' is aluminum or magnesium and a is equal to the valence of the metal M'' , a compound having the formula TiX_b , wherein X is chlorine or bromine and b is an integer from 2 to 4, inclusive, and elemental iodine, (4) a catalyst comprising an organometal compound having the formula R_xM''' , wherein R is an organo radical as defined above, M''' is aluminum, gallium, indium or thallium, and x is equal to the valence of the metal M''' , a titanium halide having the formula TiX_d , wherein X is chlorine or bromine, and an inorganic halide having the formula M^vI_c , wherein M^v is beryllium, zinc, cadmium, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorus, antimony, arsenic and bismuth, and c is an integer from 2 to 5, inclusive, and (5) a catalyst comprising an organo compound having the formula R_xM''' , wherein R, M''' and x are as defined above, titanium tetraiodide, and an inorganic halide having the formula M^vX_d , wherein M^v is aluminum, gallium, indium, thallium, germanium, tin, lead, phosphorus, antimony, arsenic or bismuth, X is chlorine or bromine, and d is an integer from 2 to 5, inclusive. The R radicals of the aforementioned formulas preferably contain up to and including 20 carbon atoms.

The following are examples of preferred catalyst systems which can be used to polymerize 1,3-butadiene to a cis 1,4-polybutadiene: triisobutylaluminum and titanium tetraiodide; triethylaluminum and titanium tetraiodide; triisobutylaluminum, titanium tetrachloride and titanium tetraiodide; triethylaluminum, titanium tetrachloride and titanium tetraiodide; diethylzinc and titanium tetraiodide; dibutylmercury and titanium tetraiodide; triisobutylaluminum, titanium tetrachloride and iodine; triethylaluminum, titanium tetrabromide and iodine; n -amylsodium and titanium tetraiodide; phenylsodium and titanium tetraiodide; n -butylpotassium and titanium tetraiodide; phenylpotassium and titanium tetraiodide; n -amylsodium, titanium tetrachloride and titanium tetraiodide; triphenylaluminum and titanium tetraiodide; triphenylaluminum, titanium tetraiodide and titanium tetrachloride; triphenylaluminum, titanium tetrachloride and iodine; tri- α -naphthylaluminum, titanium tetrachloride and iodine; tribenzylaluminum, titanium tetrabromide and iodine; diphenylzinc and titanium tetraiodide; di-2-tolylmercury and titanium tetraiodide; tricyclohexylaluminum, titanium tetrachloride and titanium tetraiodide; ethylcyclopentylzinc and titanium tetraiodide; tri(3-isobutylcyclohexyl)aluminum and titanium tetraiodide; tetraethyllead, titanium tetrachloride and titanium tetraiodide; trimethylphenyllead, titanium tetrachloride and titanium tetraiodide; diphenylmagnesium and titanium tetraiodide; di- n -propylmagnesium, titanium tetrachloride and titanium tetraiodide; dimethylmagnesium, titanium tetrachloride and iodine; diphenylmagnesium, titanium tetrabromide and iodine; methylethylmagnesium, and titanium tetraiodide; dibutylberyllium and titanium tetraiodide; diethylcadmium and titanium tetraiodide; diisopropylcadmium and titanium tetraiodide; triisobutylaluminum, titanium tetrachloride, and antimony triiodide; triisobutylaluminum, titanium tetrachloride and aluminum triiodide; triisobutylaluminum, titanium tetrabromide and aluminum triiodide; triethylaluminum, titanium tetrachloride and phosphorus triiodide; tri- n -dodecylaluminum, titanium tetrachloride and tin tetra-

iodide; triethylgallium, titanium tetrabromide and aluminum triiodide; tri- n -butylaluminum, titanium tetrachloride, and antimony triiodide; tricyclophenylaluminum, titanium tetrachloride, and silicon tetraiodide; triphenylaluminum, titanium tetrachloride, and gallium triiodide; triisobutylaluminum, titanium tetraiodide and tin tetrachloride; triisobutylaluminum, titanium tetraiodide and antimony trichloride; triisobutylaluminum, titanium tetraiodide and aluminum trichloride; triisobutylaluminum, titanium tetraiodide, and tin tetrabromide; triethylgallium, titanium tetraiodide, and aluminum tribromide; triethylaluminum, titanium tetraiodide, and arsenic trichloride; and tribenzylaluminum, titanium tetraiodide, and germanium tetrachloride.

15 The polymerization process for preparing cis-polybutadiene is carried out in the presence of a hydrocarbon diluent which is not deleterious to the catalyst system. Examples of suitable diluents include aromatic, paraffinic, and cycloparaffinic hydrocarbons, it being understood that mixtures of these materials can also be used. Specific
20 examples of hydrocarbon diluents include benzene, toluene, n -butane, isobutane, n -pentane, isooctane, n -dodecane, cyclopentane, cyclohexane, methylcyclohexane, and the like. It is often preferred to employ aromatic hydro-
25 carbons as the diluent.

The amount of the catalyst used in preparing the cis-polybutadiene product can vary over a rather wide range. The amount of the organometal used in the catalyst composition is usually in the range of 0.75 to 20 mols per
30 mol of the halogen-containing component, i.e., a metal halide with or without a second metal halide or elemental iodide. The mol ratio actually used in a polymerization will depend upon the particular components employed in the catalyst system. However, a preferred mol
35 ratio is generally from 1:1 to 12:1 of the organometal compound to the halogen-containing component. When using a catalyst comprising an organometal compound and more than one metal halide, e.g., titanium tetrachloride and titanium tetraiodide, titanium tetrachloride or
40 tetrabromide and aluminum iodide, the mol ratio of the tetrachloride or tetrabromide to the iodide is usually in the range of 0.05:1 to 5:1. With a catalyst system comprising an organometal compound, a titanium chloride or bromide and elemental iodine, the mol ratio of
45 titanium halide to iodine is generally in the range of 10:1 to 0.25:1, preferably 3:1 to 0.25:1. The concentration of the total catalyst composition, i.e., organometal and halogen-containing component, is usually in the range of 0.01 to 10 weight percent, preferably in the range
50 of 0.01 to 5 weight percent, based on the total amount of 1,3-butadiene charged to the reactor system.

The process for preparing cis-polybutadiene can be carried out at temperatures varying over a rather wide range, e.g., from -100 to 250° F. It is usually preferred
55 to operate at a temperature in the range of -30 to 160° F. The polymerization reaction can be carried out under autogenous pressure or at any suitable pressure sufficient to maintain the reaction mixture substantially in the liquid phase. The pressure will thus depend upon the particular diluent employed and the temperature at which the polymerization is conducted. However, higher pressures
60 can be employed if desired, these pressures being obtained by some such suitable method as the pressurization of the reactor with a gas which is inert with respect to the
65 polymerization reaction.

Various materials are known to be detrimental to the catalyst employed in preparing the cis-polybutadiene. These materials include carbon dioxide, oxygen and water. It is usually desirable, therefore, that the buta-
70 diene and the diluent be freed of these materials as well as other materials which may tend to inactivate the catalyst. Furthermore, it is desirable to remove air and moisture from the reaction vessel in which the polymerization is to be conducted.

Upon completion of the polymerization reaction, the

reaction mixture is then treated to inactivate the catalyst and recover the rubbery polymer. A suitable method of accomplishing this result involves steam stripping the diluent from the polymer. In another suitable method, a catalyst inactivating material, such as an alcohol, is added to the mixture so as to inactivate the catalyst and cause precipitation of the polymer. The polymer is then separated from the alcohol and diluent by any suitable means, such as decantation or filtration. It has been found to be advantageous to add an antioxidant, such as 4,4'-methylene-bis-(2,6-di-tert-butylphenol), to the polymer solution prior to recovery of the polymer. The polymer which has been recovered by these methods is then treated in accordance with the present invention so as to reduce the tendency of the polymer to cold flow.

A more comprehensive understanding of the invention may be obtained by referring to the following illustrated example which is not intended, however, to be unduly limitative of the invention.

EXAMPLE

A series of runs was carried out in which varying amounts of a trans-polybutadiene were blended with a cis-polybutadiene. The cis-polybutadiene employed in the runs was prepared by polymerizing 1,3-butadiene in the presence of a catalyst obtained by mixing triisobutylaluminum, titanium tetrachloride and free iodine. The cis-polybutadiene product contained about 95 percent cis 1,4-addition. The trans-polybutadiene used was prepared by polymerizing 1,3-butadiene with a catalyst consisting of an ether solution of lithium aluminum hydride and titanium tetraiodide. The trans-polybutadiene contained about 90 percent trans 1,4-addition.

Blending of the polymers was carried out in Banbury mixer. The dump temperature was measured in each run and the cold flow properties of the blends determined. Portions of the blended stocks were compounded in a tread recipe and the physical properties were determined. The results obtained in these runs are shown below in the table.

TABLE

Run No.	1	2	3	4	5	6	7	8	9	10	11
Cis-polybutadiene, Parts by Wt.	95	95	95	96	97	98	99	99.5	99.75	100	100
Trans-polybutadiene, Parts by Wt.	5	5	5	4	3	2	1	0.5	0.25	---	No mixing.
Banbury Dump Temp., ° F.	200	260	310	310	310	305	305	310	320	305	---
Mix Time, Min.	0.75	1.75	3.0	2.5	2.25	2.1	2.2	2.1	2.3	2.0	---
Mooney, (ML-4 at 212° F.) ²	42	40	36.5	36	38	38	38	38	38	38	40
Cold-Flow ³	3.4	2.22	1.88	2.58	3.02	3.51	3.96	4.04	3.77	4.39	5.51

COMPOUNDING AND PHYSICAL PROPERTIES

Carbon Black	50	50	50	50	50	50	50	50	50	50	50
Zinc Oxide	3	3	3	3	3	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2	2	2	2	2	2
Phirlich 5 ⁴	10	10	10	10	10	10	10	10	10	10	10
Flexamine ⁵	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
NOBS Special ⁶	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.05

PROCESSING DATA

Mooney (MS-1½ at 212° F.) ²	43.7	41.0	41.0	42.0	41.3	41.7	41.4	41.2	41.0	40.8	42.2
Extrusion at 250° F.: ⁷											
In. min.	43	38.5	35	34.8	35.8	35.2	35.0	35.0	33.5	35.0	41.5
g. min.	108	98	93	91.5	93.5	92.5	90.5	92.5	89.5	92	103
Rating (Garvey Die)	7+	7+	7+	8-	7+	8-	8-	8-	8-	8-	8-

PHYSICAL PROPERTIES (30 MIN. CURE AT 307° F.)

μ × 10 ⁴ moles/cc. ⁸	1.87	1.89	1.85	1.87	1.87	1.92	1.93	1.95	1.90	1.92	1.90
300% Modulus, p.s.i. ⁹	1,020	1,100	1,120	1,080	1,050	1,080	1,000	1,000	960	1,020	1,030
Tensile, p.s.i. ⁹	2,570	2,310	2,675	2,555	2,590	2,370	2,460	2,495	2,490	2,450	2,635
Elongation, Percent ⁹	540	480	545	530	550	480	520	510	510	510	520
Tear Strength, lb./inch ¹⁰	165	190	225	195	160	205	165	180	170	180	170
Heat Build-up, T., ° F. ¹¹	48.7	47.6	47.6	47.3	46.9	46.9	46.9	45.6	45.3	46.3	46.9
Resilience, Percent ¹²	74.4	74.6	75.9	75.3	75.9	75.3	75.8	77.2	76.4	77.7	74.4
Blowout, Min. ¹³	15.8	14.1	11.1	13.4	9.7	8.9	10.8	14.6	12.6	12.8	13.8
Shore A Hardness ¹⁴	60.0	59.5	59.0	58.5	58.5	59.0	58.5	59.0	58.5	58.5	59.0

¹ The temperature of the blend upon completion of the mixing operation.

² ASTM D-297-55T.

³ Cold-Flow—Glass Plate Method. Method is based on the change in contact area of four right circular cylinders of rubber compressed between two glass plates. The cold flow rating is the ratio of the final contact area to the original contact area. Four pellets, approximately 0.450 inch in diameter and the same in height, are measured with a hand micrometer and recorded as thousandths of an inch. The average diameter is obtained and squared. Glass plates 3" x 4" weighing an average of 26-27 grams, which have been cleaned and polished with silicone lens tissues, are used for the test. Four rubber pellets are positioned at the corner of 1.5" x 2" rectangle within the glass plate. Another glass is positioned over the top of the pellets such that it is directly over the bottom plate and a 160 gram 3" x 4" lead plate is placed on top. The assembly is allowed to stand 18 hours at 80° F. after which the lead weight is removed and the contact area observed through the glass plate. Measurement is first taken across the longest dimension of the contact area and a second measurement taken at right angles to the first one. The eight measurements (two for each pellet) are recorded and averaged to obtain a final average diameter. The value is squared and divided by the initial average diameter squared to obtain the cold flow.

⁴ Aromatic oil.

⁵ Physical mixture containing 65 percent of a complex diarylamineketone reaction product and 35 percent of N,N'-diphenyl-p-phenylenediamine.

⁶ N-oxyl-diethylene-2-benzothiazyl sulfenamide.

⁷ Extrusion is carried out at 250° F. by essentially the same procedure as described by Garbey et al., Inc. & Eng. Chem. 34, 1309 (1942). As regards the rating figure, 12 designates an extruded product considered to be perfectly formed whereas lower numerals indicate less perfect products.

⁸ Determined by the swelling method of Kraus as given in Rubber World, October, 1946. This value is the number of effective network chains per unit volume of rubber. The higher the number, the more the rubber is crosslinked (vulcanized).

⁹ ASTM D412-51T. Scott Tensile Machine L-6. Tests made at 80° F.

¹⁰ ASTM D624-54, Die A.

¹¹ ASTM D623-52T. Method A, Goodrich Flexometer, 143 lbs./sq. in. load, 0.175 inch stroke. Test specimen is a right circular cylinder 0.7 inch in diameter and 1 inch high.

¹² ASTM D945-55(modified). Yerzley oscillograph. Test specimen is a right circular cylinder 0.7 inch in diameter and 1 inch high.

¹³ Goodrich Flexometer, 257 lbs./sq. in. load, 0.250 inch stroke, 200° F. oven temperature. Reported as running time to failure of test specimen.

¹⁴ ASTM D676-55T. Shore Durometer, Type A.

The data in the foregoing table show that a substantial reduction in the tendency of cis-polybutadiene to cold flow is obtained by blending the polymer with a small amount of trans-polybutadiene. The physical properties of the vulcanizates were good at all levels, reaching a maximum in most instances at the point of greatest lowering in cold flow. Incorporation of the small amounts of trans-polybutadiene did not adversely effect the physical properties of the cis-polybutadiene, and in many instances actually improved certain properties.

The composition of this invention is suitable for all uses for which the cis-polybutadiene per se can be employed. It is particularly useful in the manufacture of tire treads, tire carcass stocks, and other rubbery articles. It can be extruded, reinforced with conventional reinforcing agents, blended with other polymers, such as natural and synthetic rubbers, extended with conventional extender oils, and vulcanized using recipes that are well known in the rubber art.

As will be evident to those skilled in the art, many variations and modifications of the invention can be practiced in view of the foregoing disclosure. Such variations and modifications are believed to come within the spirit and scope of the invention.

I claim:

1. A rubbery, unvulcanized composition of matter comprising a blend of (1) a cis-polybutadiene containing at least 85 percent cis 1,4-addition, and (2) from 0.1 to about 5 parts by weight of a trans-polybutadiene per 100 parts by weight of said cis-polybutadiene and said trans-polybutadiene said trans-polybutadiene containing at least 70 percent trans 1,4-addition.

2. The composition of claim 1 in which said cis-polybutadiene contains from 85 to 98 percent cis 1,4-addition and said trans-polybutadiene contains from 70 to 95 percent trans 1,4-addition.

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