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TREATMENT OF POLYBUTADIENE

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This invention is concerned with a process for treating polybutadiene to improve its processibility. In particular, it is concerned with adding certain amines to polybutadiene having at least about twenty-five percent (25%) cis-1,4 configuration so that the plasticity of the material is reduced and it may be processed more readily. It should be emphasized that, by means of the present invention, the plasticity is reduced while other physical properties are not impaired, but are in some cases improved.

The present invention is useful in the treatment of stereospecific polybutadiene containing at least about twenty-five percent (25%) cis-1,4 configuration. The plasticity of a polymer is a function of several factors, among which may be mentioned molecular weight, molecular weight distribution, and various inter- and intramolecular forces. The amine additives of the present invention are believed to exert their influence by modifying the molecular forces, characteristic of cis-1,4 polybutadiene in the solid state, due to packing of the molecular chains.

The term "plasticity" is defined in the American Society for Testing Materials' Special Technical Publication No. 184 as being:

> "The property possessed by certain solid materials of keeping the shape or form imparted to them by a deforming force. It is characterized by a complete lack of elasticity and may be regarded as a state of matter in which internal friction and tendency to flow balance each other."

The plasticity of a polymer may be measured in several ways, the most common method in the United States being the use of a Mooney viscometer. The use of this instrument is described in the A.S.T.M. Standards of 1958, part 9, A.S.T.M. designation D–927–57T. The measure of plasticity obtained by using the Mooney viscometer is referred to as the Mooney viscosity.

When a material has a high Mooney viscosity, it is difficult to process. In particular, it is difficult to mill it or to extrude it. The present invention solves this problem by providing a method for lowering the Mooney viscosity of cis-1,4 polybutadiene. Furthermore, material treated according to the present invention emerges from a Garvey die with a much better rating than untreated material. (The Garvey die extrusion test is also described in A.S.T.M. Special Technical Publication No. 184.) The treated material emerges from the Garvey die test with improved surface, edges, corners and contours.

Prior to the present invention it was often necessary to incorporate natural rubber with cis-1,4 polybutadiene in order to obtain material which could be readily processed. It is one of the very important advantages of the present invention that the use of natural rubber is no longer required for this purpose.

Conventional cis-1,4 polybutadiene can not be milled on a roll mill at high temperatures without great difficulty. By the use of the present invention there are obtained materials which can be successfully and easily milled at much higher temperatures. The invention therefore makes is possible to manufacture cis-1,4 polybutadiene having a Mooney viscosity low enough to be consistent with easy processing, but having wear resistance and other desirable properties in no way impaired.

The additives employed in the present invention are primary or secondary amines containing at least six carbon atoms. The amines may be aliphatic, aromatic, cyclic, saturated or unsaturated. Both mono and diamines may be used. Best results have been obtained with unsaturated compounds. In general, primary amines are more effective than secondary amines. Particularly good results have been obtained using 1-aminooctadecene-9. As examples of other amines which are useful in the present invention, there may be mentioned 1-aminooctadecane, dehydroabietyl amine, dodecyl amine, octyl amine, hexyl amine, distearyl amine, dipalmetyl amine, dihexyl amine, and oleic-1,3-propylenediamine (which may also be used in the form of its mono- and di-oleates). This last named amine is representative of a class of N-alkyl trimethylene diamines. Amines of this class give particularly good results, especially when the alkyl group contains from 12 to 18 carbon atoms.

In carrying out the process of the present invention, the amine is mixed with the cis-1,4 polybutadiene at some stage after the desired degree of polymerization has taken place. This may be conveniently accomplished while the polymer is in the reaction solution in which it has been made. The treated polymer is then recovered by conventional procedures. Although experimental evidence is not yet conclusive, in some cases an additional advantage of the invention may be obtained by using an unsaturated amine as a "shortstop" to the polymerization reaction which forms the polybutadiene. This would result in eliminating the need to use a conventional "shortstop" which does not improve processibility.

The amount of amine to be added varies considerably. Some amines are more effective than others, and some samples of polybutadiene require more amine than others. In general, it may be said that where the polybutadiene has a relatively low Mooney viscosity to start with, less amine will be required to bring about a noticeable reduction in the Mooney viscosity. For example, as little as 0.2 of a percent may give an appreciable result. On the other hand, polybutadiene samples which initially have a high Mooney viscosity require more amine to bring about an appreciable lowering of the Mooney viscosity. As much as 1% amine may be required in some cases. Percentages are stated by weight based on the amount of polybutadiene.

It has been observed that in general the lowering of the Mooney viscosity reaches a maximum when a particular amount of amine has been added, and the subsequent addition of still more amine causes no more lowering of the Mooney viscosity. For most purposes, the optimum amount of amine to be added can be stated as being from, roughly, two or three percent up to several percent. In the case of samples having a very high initial Mooney viscosity as much as ten percent may be used.

The following examples are given solely for purposes of illustration and are not to be deemed as limitation of the present invention, many variations of which well occur to those skilled in the art without departing from the spirit or scope thereof.

Example 1

200 grams of polybutadiene, containing approximately 95% cis-1,4 configuration, and having a Mooney viscosity at 212° F. of 42, was dissolved in approximately 3½ liters of toluene. 6 grams of oleyl amine was then added to the polymer solution. The solution was stirred by hand. Steam was then injected into the mixture until nearly all of the toluene had been stream distilled, after which the polymer-amine mixture was dried on a hot

roll mill at approximately 200° to 220° F. The Mooney viscosity at 212° F. of the treated polymer was 28.

It is thus seen that the Mooney viscosity was lowered from 42 in the untreated material to 28 in the treated material. All Mooney viscosities are base on large rotor readings.

Example 2

200 grams of polybutadiene, containing approximately 95% cis-1,4 configuration, and having a Mooney viscosity at 212° F. of 46, was dissolved in approximately 3½ liters of toluene. 6 grams of dehydroabietyl amine was then added to the polymer solution. The solution was mixed thoroughly by hand stirring. Steam was then injected into the mixture until nearly all of the toluene had been removed, after which the polymer-amine mixture was dried on a hot roll mill at approximately 200° to 220° F. The Mooney viscosity at 212° F. of the treated polymer was 33½.

In order to show further the effect of dehydroabietyl amine on the polybutadiene sample treated above, Garvey die data at 180° F. were obtained on the untreated raw polymer containing 50 parts high abrasion furnace carbon black (HAF), and on the treated raw polymer containing three percent (3%) dehydroabietyl amine and fifty (50) parts HAF carbon black. The Garvey die readings are reported in the following table:

	Treated Sample	Untreated Sample
Edge	3.5	1.0
Corners	3.5	2.0
Surface	2.5	0.5
Contour	2.5	1.0
Total points, 16 maximum	12.0	4.5

It thus is seen that the treated polybutadiene scored better than the untreated material in every part of the test.

Example 3

Using the procedures of the foregoing examples, tests were run on many samples of polybutadiene, using various amines as additives. The tested polybutadienes included materials varying from about twenty-five percent (25%) to iniety-eight percent (98%) in their content of cis-1,4 configuration. In all cases it was found that, when a primary or secondary amine containing at least six carbon atoms was added in an amount from few tenths of a percent to several percent, the Mooney viscosity was lowered and the Garvey extrusion index was increased.

What is claimed is:

A process for lowering the plasticity of polybutadiene containing at least twenty-five percent cis-1,4 configuration, said process consisting essentially of incorporating in a solution of the polybutadiene a small but effective amount of dehydroabietyl amine.

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