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3,278,472

STABILIZATION OF POLY- α -OLEFINS BY ASPHALTIC SUBSTANCES

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No Drawing. Filed May 12, 1960, Ser. No. 28,538

2 Claims. (Cl. 260—28.5)

This invention relates to the stabilization of poly- α -olefins, including polyethylene and polypropylene, by incorporating therein a minor proportion of a hydrocarbon pyrolysate, such as various asphalts, tars and pitches.

An object of the present invention is to provide poly- α -olefin compositions stabilized against damage from heat, sunlight and weather.

Other objects will appear hereinafter.

In accordance with the present invention, these and other objects are attained by homogeneously mixing a poly- α -olefin with a minor proportion of a pyrolysate of the class consisting of asphalts, bitumens, tars and pitches. These pyrolysates stabilize the poly- α -olefins, including polyethylene and polypropylene, against the deteriorating effects of heat, sunlight and weather. The range of concentration of the pyrolysates in the poly- α -olefins which will impart desirable heat stability and weathering stability thereto is from 0.1 to 10% by weight. We have further found that the weathering stability appears to be dependent on the sulfur content of the asphaltic material.

The present invention is further illustrated in the following examples.

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210° F. It showed a brown background color but also showed some large specks of undispersed asphalt. However, the well-dispersed portion of the asphalt was sufficient for stabilization purposes. When heated in the oven for 105 hours at 140° C., this sample showed no measurable peroxide formation. By contrast, a sample of the same polyethylene without stabilizer developed peroxides in seven hours and a sample containing 3% carbon black, but no asphalt, dispersed therein developed peroxides in 15 hours.

Example 3

Table I gives the weather abilities of polyethylene containing various asphaltic pyrolysates milled into the plastic according to the conditions given in Example 1.

Plates 1/8 inch thick were compression-molded, cut into 1 1/2 x 1/2 inch strips, bent into a U-shape and exposed to natural weathering at Kingsport, Tennessee. These stressed specimens were inspected periodically for the onset of visible cracking. Similar specimens containing no asphalt were included for comparison.

The great variation in stabilizing behavior exhibited by the different varieties of asphalt is distinctly surprising and unexpected. For of the asphalts tested actually decreased the weatherability of the polyethylene, although the heat stability was improved by their presence. These differences may be understandable on the basis of the sulfur analyses of the asphalts which are also shown in Table I. A direct correlation between weatherability of the plastic and sulfur content of the asphalt is shown in the table. An asphaltic addition which contains from 2 to 6% sulfur appears to improve weatherability.

TABLE I.—WEATHERABILITY OF POLYETHYLENE CONTAINING ASPHALTIC MATERIALS

Asphaltic Material	Supplier	Percent By Weight	Stress-Cracking Resistance, Exposure Time (Days) Required to Start Cracking in—			Sulfur Content of Asphalt, Percent By Weight	Appearance After 561 Days' Exposure
			First Sample	Half the Samples	All Ten Samples		
None.			330	339	367		
Super Selects Gilsontite.	Allied Asphalt and Mineral Corp.	3	275	280	287	0.17	Dull, badly cracked. Semi-dull, very badly cracked, whitish where stressed.
12421 Asphalt.	Socony-Vacuum Oil Co.	3	285	290	295		Dull, finely cracked.
12420 Asphalt.	do.	3	293	298	303	1.14	Semi-dull, finely cracked.
E6103 Pitch.	Witco Chemical Co.	3	295	300	303	1.37	Dull, finely cracked.
Noah's Pitch.		3	611	611	630		Dull, uncracked.
Dead-Level Asphalt.	Johns-Manville Corp.	3	654	660	711	2.90	Shiny, uncracked.
B-6114 Asphalt.	Socony-Vacuum Oil Co.	3	659	680	743	4.72	Do.
B-6312 Asphalt.	do.	3	687	742	1,002	3.84	Do.
Roofing Asphalt 190.	Johns-Manville Corp.	3	751	765	1,035	5.88	Dull, uncracked.

Example 1

Polyethylene of melt index 7 was rolled between a pair of milling rolls for six minutes with three parts of weight of roofing asphalt sold in the trade as Johns-Manville roofing asphalt No. 190. The front roll temperature was 240° F. and the back roll temperature 215° F. Front: back roll speed ratio was 4:3. Microscopic examination at 100X magnitude revealed the absence of resolvable particles. When heated at 135° C. for 100 hours, no peroxide formation was noted.

Example 2

A composition similar to the first-mentioned formulation of Example 1, but containing 10% by weight of the same asphalt, was rolled for 10 minutes with a front roll temperature of 260° F. and a back roll temperature of

Example 4

Some of the compositions listed in Table I were heated in a mechanical convection air oven at 160° C. until peroxides were chemically detectable. The peroxide induction periods, taken to be measures of heat stability, are shown in Table II. Also included for comparison are several similarly compounded polyethylene compositions containing 3% of various carbon blacks.

The data of Table II show clearly the superiority of the asphalts over the carbon blacks as heat stabilizers for polyethylene. Sulfur content of the asphalt appeared to have little effect on its activity as a heat stabilizer. This is in marked contrast to the effects observed in weathering.

TABLE II.—HEAT STABILITY OF POLYETHYLENE CONTAINING ASPHALTIC MATERIALS

Stabilizer	Percent By Weight	Oven Life at 160° C. [Time (hr.) for Initiation of Peroxides]
None		1.5
12420 Asphalt	3	60
Dead-Level Asphalt	3	60
B-6312 Asphalt	3	60
B-6114 Asphalt	3	60
Super Selects Gilsonite	3	60
Pitch E6103	3	60
Roofing Asphalt 190	3	60
Carbon Blacks:		
Sterling R.	3	6
Witco 32	3	6
Vulcan XC-72	3	11
Witco 100	3	17
Superba Beads	3	19

Example 5

High density polyethylene (density=0.955) was heated in air at 160° C. Peroxides formed in less than 1 hour. The same polyethylene containing 3% by weight of Roofing Asphalt 190 showed no peroxide after 32 hours' heating under the same conditions. The asphalt was roll-compounded into the polyethylene as described in Example 1 except that front roll temperature was 290° F. and the rear roll 250° F.

Example 6

Isotactic polypropylene powder (density=0.915) was mixed with 3% of its own weight of Roofing Asphalt 190 added in toluene solution. After evaporation of the toluene, the plastic was injection-molded in the form of tensile bars 2.5 in. long by 0.062 in. thick. These bars, bent into U-shape, were mounted in an air oven maintained at 130° C. Similar samples of unstabilized isotactic polypropylene were exposed in the same way. The latter became brittle and cracked in 6 hours. The stabilized samples, however, were still uncracked and tough after 220 hours.

Example 7

The asphalt-containing isotactic polypropylene composition of Example 6 was heated in an oven at 160° C. along with an unstabilized control sample. Peroxides formed in the control sample within 15 minutes. The stabilized sample required 40 hours to reach the same stage of oxidation.

Polyolefins stabilized with pyrolysates in accordance

with this invention may be used in various ways. In extrusion molding operations, more pounds per hour may be extruded into tubes or sheeting with less degradation of the plastic during the hot extrusion operation. We have observed that replacing all or a portion of the carbon black normally employed in stabilizing olefins with the above-described desirable asphaltic substances eliminates the disadvantageous formation of gases due to excess carbon black during the extrusion operation.

The molded polyolefins may be employed in the form of various articles which are to be exposed to outside weather conditions.

Using the suggested asphaltic stabilizers, a masterbatch of suitable low melt viscosity for efficient dilution with unpigmented polyolefins may be prepared.

We claim:

1. Heat and weather stabilized polypropylene comprising polypropylene and 0.1 to 10% of a pyrolysate containing from about 2% to 6% sulfur selected from the group consisting of asphalts, bitumen, tars and pitches.

2. Heat and weather stabilized polypropylene comprising polypropylene and 0.1 to 10% by weight of asphalt containing 2 to 6% sulfur.

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