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[54] **PLASTISOLS AND GASKETS**

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[57] **ABSTRACT**

Plastisols, preferably of polyvinyl chloride, having a high yield value and low high shear viscosities are obtained by thickening conventional plastisol preparations with about 1 to 40 parts of certain block copolymers of the A-B-A type in which B is an elastomeric polymer core and A stands for a thermoplastic polymerized alkenyl aromatic compound. Tough, resilient gaskets can be manufactured from these improved materials.

3 Claims, No Drawings

PLASTISOLS AND GASKETS

THE PRIOR ART

In the bottling of carbonated beverages, an air-tight pressure crown seal is applied on the orifice of the container, for instance a bottle, to retain the carbonation of the contents and to protect the beverage against contamination. Crowns for such bottles are made of metal having uniform ductility, gage and even temper and are lined with a sealing gasket which may consist of cork, polyethylene, fluxed plastisols or other plastic materials. It is with fluxed plastisol linings or gaskets of this general type that the present invention is concerned.

Basically, plastisols comprise a dispersion of finely divided thermoplastic resin particles in a liquid non-volatile plasticizer in which the resin is insoluble or only very slightly soluble at room temperature. At elevated temperatures, the resin becomes substantially completely solvated by the plasticizer, yielding a homogeneous solution which transforms itself into a rubbery thermoplastic mass upon cooling. In addition to the basic components, other ingredients may enter the plastisol compositions to accomplish conventional purposes. Thus the compositions may contain fillers, pigments, stabilizers, wetting agents and thickeners. Also, when a fluxed cellular liner is desired, a gas may be dispersed in the plastisol or a gas-evolving agent, i.e., a blowing agent, may be incorporated which will decompose at the fluxing temperature of the composition.

Plastisols are widely used in the manufacture of sealing gaskets for crown closures, where the gasket comprises an over-all liner coextensive with the inside surface of the closure panel. According to one method of lining closures, a measured quantity of plastisol is deposited in an inverted closure shell and the closure is rotated at high speed to cause the deposit to spread over the inner surface of the closure panel. The deposit is then heated at a temperature and for a period of time sufficient to completely flux the composition. In bottle-capping operations, the lined crown closure thus obtained is placed over the orifice of the bottle and the skirt of the crown is crimped around the locking ring of the bottle to form a seal.

The operations and manipulations that the plastisols must undergo in the procedures just described and in other similar sealing applications require that the liquid compositions involved possess certain characteristic rheological properties. The compositions must be fluid enough at high shear rates to permit easy disposition through a nozzle and rapid distribution over the inner surface of the closure when the spin lining technique is employed. Yet, they must possess a viscosity sufficiently high so that the gasket material remain in position until it is solidified by heat treatment. This type of property is conventionally imparted to plastisols by incorporating into them a small quantity of a finely divided material, generally of siliceous nature.

It is an object of this invention to provide improved plastisol preparations which yield tougher closure gaskets that can better survive the abuse to which such closures are conventionally subjected in their ultimate application. It is also an object of this invention to provide plastisols possessing a more easily controlled thixotropy than that of conventional materials. Another object is to prepare plastisols capable of yielding seal-

ing gaskets of increased shear and tensile modulus under high strain and of lesser hardness than normally available. A further object is to provide fluxed plastisols that are more resistant to extraction of their plasticizer by certain organic liquids to which they may be exposed.

SUMMARY OF THE INVENTION

It has now been discovered that the yield value of unfluxed plastisols, i.e., the low shear viscosity, can be successfully increased, without significantly affecting the high shear viscosity, by incorporating into the plastisols relatively small quantities of certain thermoplastic elastomeric block copolymers of conjugated dienes with certain alkenyl aromatic comonomers, dissolved in conventional plasticizers. It has also been discovered that sealing gaskets obtained from plastisols of this type will be stronger, more resilient and softer than those obtained from plastisols containing conventional siliceous materials.

While the quantity of block copolymer that will achieve desirable improvement will vary with such factors as the nature and molecular weight of specific block copolymers, the plasticizer contents of the composition and the particular application contemplated, the preferred proportions lie within the range of about 5 to 25 parts by weight of block copolymer per 100 parts of plastisol resin. However, useful compositions may be devised with as little as 1 part and as much as 40 parts of copolymer per 100 parts thermoplastic resin.

DETAILED DESCRIPTION

The block copolymers that are added to plastisols according to the present invention are thermoplastic elastomers composed of polymerized alkenyl substituted aromatic segments attached to the ends of an elastomeric polymerized hydrocarbon chain core. Usable hydrocarbon monomers for forming the core preferably contain four to eight carbon atoms. This includes butadiene, isoprene, pentadiene-1,3 and 2,3-dimethylbutadiene. The elastomeric core material may also consist of saturated ethylene-propylene copolymers. The alkenyl aromatic hydrocarbon monomers used to form the rest of the block copolymer molecule are preferably of the monovinyl substituted type such as styrene, methylstyrene, vinyl toluene, vinyl naphthalene and the like. More than one monomer may be employed for each section of the block copolymer.

The structure of the block copolymers being described may be represented by the formula A-B-A in which B is the elastomeric core while A stands for the aromatic alkene polymer segments. While, obviously such copolymers may possess a gradation of properties ranging from those of relatively homogeneous polymerized aromatic vinyl compounds to those of relatively homogeneous elastomers, the polymers of particular interest here possess a thermoplastic segment content of about 10 to 50 percent by weight, an average elastomeric core molecular weight of about 10,000 to 200,000, and an average thermoplastic segment molecular weight of 2,000 to 30,000. The preferred copolymers within the class just described are styrene-butadiene block copolymers containing from about 25 to 30 percent by weight polymerized

styrene and having an average overall molecular weight of between about 60,000 and 160,000.

To carry out the invention, as mentioned earlier, the selected copolymer is dissolved in a conventional liquid plasticizer and the solution is incorporated into the plastisol by mixing. Between about 1 and 40 parts by weight of block copolymer per hundred parts of plastisol resin will yield the desired results.

The plasticizers that may be employed to dissolve the block copolymer as well as to form the plastisol may be dialkyl phthalates, such as dioctyl phthalate, butyl decyl phthalate and octyl decyl phthalate; alkyl phthalyl alkyl glycolates, such as butyl phthalyl butyl glycolate and methyl phthalyl ethyl glycolate; and dialkyl esters of alkane dicarboxylic acids, such as dioctyl and dibutyl sebacates, dioctyl azelate and diisobutyl adipate. Secondary plasticizers that may be incorporated in the plastisol include trialkyl and triaryl phosphates, acetyl trialkyl citrates, alkyl esters of high fatty acids, epoxy derivatives and polymeric polyester plasticizers, such as glycol sebacate polyesters. If desired, mixtures of plasticizers may be employed including one or more primary plasticizers and blends of primary and secondary plasticizers.

The following examples are given to illustrate the practice of the invention.

EXAMPLE 1

A block copolymer preflux is formed by heating with agitation at 250° to 280°F, one part by weight of a block copolymer of styrene and butadiene containing 25 percent bound styrene and having an average overall molecular weight of about 120,000, with 4 parts dioctylphthalate.

A conventional polyvinyl chloride (PVC) plastisol is prepared from the following ingredients:

	Parts by weight
PVC resin, plastisol grade	100
Dioctylphthalate (DOP)	50
Azodicarbonamide, 33% in DOP	1.08
Zinc/calcium stearates in epoxidized soybean oil (stabilizer)	0.5
Eicosane	4
Paraffin wax, melting range 120°-131°F	3
Block copolymer preflux, 20% concentration	25

A wax-plasticizer blend is formed by melting the wax in a few parts of the plasticizer at a temperature of approximately 130°F. The hot wax blend is mixed with about half the plasticizer, the mixture stirred and allowed to cool to about 110°F. The eicosane, the stabilizer, the azo compound and the resin are added with stirring. The remaining plasticizer is also added and the resulting composition stirred until a homogeneous mixture results. The preflux is then blended in to obtain a product having a 60 rpm viscosity of 14,000 centipoises and a 6 rpm viscosity of 45,000 cps as measured on a Brookfield viscosimeter (model LVF-SX) at 110°F with a No. 3 spindle.

EXAMPLE 2

A plastisol is prepared as in Example 1 except that it contains 3 parts of fumed silica, a conventional thickener. The SBR block copolymer preflux is omitted.

The plastisol thus obtained has a 6 rpm viscosity of 60,000 cps and a 60 rpm viscosity of 20,000 cps.

The plastisols of Example 1 and 2 were applied to bottle crowns and fluxed in the conventional manner. The crowns were then affixed to bottles filled with simulated soft drink pack and the packages obtained were subjected to an abuse test.

In this test, a static load pressure of 100 lbs is applied to capped bottles and maintained constant for a period of one week. This treatment duplicates conditions found in soft drink bottling plants where cases of packed soda are stacked on top of one another with the weight of the upper cases being applied to the bottle crowns in the lower cases. After one week, the static pressure is released. The carbon dioxide pressure retained in each bottle is measured, 24 hours after release, by means of a head sampler and a pressure gauge. The results are recorded in terms of gas volumes, 4.0 gas volumes indicating a perfect performance since that is the amount of gas originally charged into the bottles. A 3.8 gas volume retention is considered acceptable by the industry, while ratings below 3.8 failures. One failure in a sample of six bottles suffices to rule a compound unsatisfactory.

The essential properties of the plastisols of Examples 1 and 2 as well as the performance of crowns sealed with them under static load abuse are summarized in the following table:

ABUSE TEST RESULTS

Example	1	2
Thickener	SBR Block Copolymer	Silica gel
Viscosity:		
6 rpm	45,000	60,000
60 rpm	14,000	20,000
6/60 ratio	3.2	3.0
Abuse Data:		
No. of failures/6 bottles	0	5
Average gas volumes	4.02	3.35

It becomes apparent from these results that SBR block copolymer reinforced plastisols show increased resistance to static load abuse as compared to the conventional silica thickened materials.

EXAMPLE 3

Another illustrative composition can be prepared in the conventional manner from the following ingredients:

	Parts by weight
PVC resin, plastisol grade	100
Dioctyl phthalate	105
Paraffin wax	4.6
Diatomaceous earth	3.5
Azodicarbonamide	0.7
Zinc oxide	0.6
Titanium dioxide	5.6
Hematite	0.16
Limonite	0.13
Carbon black	0.03

To this plastisol is added 20 parts of a 15 percent preflux of an isoprene-styrene block copolymer having an average core molecular weight of 200,000 and an average styrene segment molecular weight of 30,000. The resulting unfluxed plastisol has a 110°F viscosity of

about 10,000 cps at 6 rpm and about 3,400 cps at 60 rpm. When fluxed and subjected to the static load abuse test described earlier, it behaves substantially as the preparation of Example 1 in that the average gas volume retained in 6 sample bottles is at least 3.8 after a 4 volume charge.

EXAMPLE 4

A fluxed plastisol with greatly decreased compressive modulus and only moderately increased shear strength, thus particularly suited for sealing and capping without any decrease in blow-off pressure, is prepared by incorporating 25 parts per 100 parts resin by weight of a styrene-butadiene block copolymer such as Kraton* (*Registered trademark, Shell Chemical Co.) 1102 which has a Brookfield viscosity of about 1000 cp at room temperature for a 25 percent concentration by weight in toluene. A 50 percent by weight solution of the block copolymer in the plasticizer is prepared by prolonged stirring and heating, for instance at 280°F, and this solution is added to a plastisol which has otherwise been prepared in the conventional manner.

A representative formulation would thus appear as follows:

	Parts by Weight	
	Total	Plasticizer
PVC resin, plastisol grade	400	—
PVC resin, suspension polymerized	100	—
Epoxydized soybean oil	25	25
Azodicarbonamide, 33%	7.5	5
Zinc oxide, 20%	15	12
Diocetyl phthalate (DOP)	258	258
Block copolymer	250	125
Total	1055.5	425

Solutions or suspensions of the various ingredient in DOP are first prepared at the solids concentration indicated and the resulting mixtures are combined in the proportions indicated in the "total" column of the above table. The block copolymer solution is added last to a thorough mixture of all the other components and it is mixed in until a uniform product is obtained. The net amount of plasticizer used is tabulated in the next column and adds up to 425 parts by weight for a final ratio of 85 parts per 100 parts resin.

For comparison purposes, a similar preparation can be made without the 125 parts styrene-butadiene block copolymer. A silica aerogel, 45 parts by weight is used instead; all other component quantities and ratios are maintained unchanged including the DOP to resin ratio.

Both formulation yield thixotropic mixtures with viscosities too high for measurement by ordinary means. On lining closures with 400 mg of these plastisols and fluxing for 3 minutes at 410°F, a number of interesting differences can be observed.

For instance, the block copolymer-containing structures have been found to possess an average 15 second

blow-off pressure 17 psi higher than their silica-containing analogs over the range of 32° to 212°F. Also, in the closing or capping operation, the closing force required for the block copolymer plastisol is only 50 to 70 percent of that needed with the conventional silica preparations. Furthermore, exposure of fluxed gaskets to 50 percent aqueous solution of ethyl alcohol at 100°F results in a loss of only 8 percent of the plasticizer when the block copolymer is present while 18 percent of the plasticizer is extracted with silica present. In general, the use of block copolymers results in increased shear and tensile modulus while providing relatively lower durometer values.

The plastisol compositions that can benefit from the incorporation of block copolymers of the styrene-butadiene type as described in this invention are those of vinyl chloride homopolymers as well as copolymers containing up to 20 percent of vinyl acetate. Although such polymers are preferred, other acid-resistant thermoplastic resins may be used, including polyvinyl acetate, polyvinyl butyrate, polyvinyl alcohol, polyvinylidene chloride, and so on. These materials, as well as the other modifying components of the plastisols such as blowing agents, fillers, stabilizers, pigments and dispersing agents are well known to the art and are listed in numerous publications including, for example, U. S. Pat. No. 3,447,710. No need exists therefore for re-numerating all the possible elements that can be combined by the man skilled in the art to yield compositions that can be improved in the manner disclosed by the present invention.

What is claimed is:

1. A container closure comprising a flowed-in gasket consisting of a fluxed layer of a plastisol of a resin selected from the group consisting of homopolymers and copolymers of vinyl chloride containing up to 20 percent of vinyl acetate, containing, for each 100 parts by weight of the resin, from about 1 to 40 parts of a block copolymer having an A-B-A structure in which B represents an elastomeric core of polymerized diene units selected from the class consisting of conjugated diene hydrocarbon compounds having four to eight carbon atoms and elastomeric copolymers of ethylene with propylene, said core having an average molecular weight within the range of 10,000 to 200,000, and A represents a thermoplastic segment of a polymerized alkenyl aromatic compound of average molecular weight within the range of about 2,000 to 30,000, wherein the total polymerized alkenyl aromatic compound content constitutes from about 10 to 50 percent by weight of the block copolymer molecule.

2. The container closure of claim 1 wherein the plastisol contains about 5 to 25 parts by weight of a copolymer of styrene and butadiene having average over-all molecular weight of about 60,000 to 160,000 and a copolymerized styrene content within the range of 25 to 30 percent of the weight of the molecule.

3. The container closure of claim 1 wherein in the block copolymer the diene unit of the elastomeric segment is derived from isoprene.

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