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<p>(21) International Application Number: PCT/EP97/01906 (22) International Filing Date: 15 April 1997 (15.04.97) (30) Priority Data: 96302632.3 16 April 1996 (16.04.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: GERARD, Eric-Jack; Avenue Jean-Monnet 1, B-1348 Ottignies (BE). DE KEYZER, Noël, Raymond, Maurice; Avenue Jean-Monnet 1, B-1348 Ottignies (BE). MENSEN-VEURINK, Jacqueline, Margaretha; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DE VLIET, Birgitte, Maria, Ludovica, Christine; Avenue Jean-Monnet 1, B-1348 Ottignies (BE).</p>	<p>(81) Designated States: BR, CN, KR, TR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>	
<p>(54) Title: STYRENE-ISOPRENE-STYRENE TRI BLOCK COPOLYMERS WITH ADAPTED DIBLOCK COPOLYMERS</p>		
<p>(57) Abstract</p> <p>Hot melt adhesive compositions comprising: (a,1) from 75-90 parts by weight of a triblock copolymer A₁B₁A₂ where A₁ and A₂ represent predominantly poly(monovinyl aromatic) blocks of the same or different peak molecular weight in the range of from 5,000 to 20,000 g/mol, wherein B₁ represents a predominantly poly(isoprene) block while the average apparent molecular weight of the total triblock copolymer is in the range of from 160,000 to 250,000 g/mol, and the monovinyl aromatic monomer content is in the range of from 15 to 25 wt.%; (a,2) from 10 to 25 parts by weight of a diblock copolymer A₃B₂, wherein A₃ represents a predominantly poly(monovinyl aromatic) block having a peak molecular weight in the range of from 5,000 to 20,000 g/mol, and wherein B₂ represents a poly(isoprene) block having an average apparent molecular weight calculated from GPC measurements which is from 80 to 110 % of the average molecular weight calculated from GPC measurements of block B₁, and wherein the monovinyl aromatic monomer content is in the range of from 5 to 17 %; (b) from 50 to 400 parts by weight of a tackifying resin; (c) from 0 to 100 parts by weight of a plasticiser and/or softening agent.</p>		

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STYRENE-ISOPRENE-STYRENE TRI BLOCK COPOLYMERS
WITH ADAPTED DIBLOCK COPOLYMERS

The invention relates to styrene-isoprene-styrene triblock copolymers with adapted diblock copolymers and to adhesive, sealant and coating compositions comprising them. More particular the invention relates to tailor made triblock copolymers-diblock copolymers, containing different molecular weight blocks from predominantly isoprene, and to hot melt adhesives, especially for use in packaging tape formulations.

Block copolymer blends of triblock copolymers and diblock copolymers comprising different molecular weight blocks are known from e.g. US patent no. 5,089,550. Said patent discloses a block copolymer composition, comprising a block copolymer composition for use in adhesives, comprising 50-85% by weight of a block copolymer A₁-B₁ from an aromatic vinyl compound and preferably styrene, and a conjugated diene and preferably isoprene, respectively, A₁ being <20% by weight of (A₁+B₁), A₁ and B₁ having a molecular weight >12,000 and >150,000, respectively; and 15-50% by weight of a block copolymer A₂-B₂-A₃ from an aromatic vinyl compound, a conjugated diene and aromatic vinyl compound, respectively, A₂+A₃ being >20% by weight of A₂+B₂+A₃, A₂ and A₃ having a molecular weight >12,000 and (molecular weight of B₂) ≤ (molecular weight of B₁)/1.5.

In addition, from e.g. US patent no. 5,405,903 a process is known for preparing block copolymer blend compositions which process comprises the subsequent steps of polymerising vinyl aromatic monomer (e.g. styrene) adding conjugated diene monomer (e.g. isoprene) to the polymerisation mixture, adding

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additional initiator, adding a second portion of conjugated diene monomer, adding a second portion of vinyl aromatic monomer and adding a terminating agent.

Said process provides a block copolymer composition, consisting of a blend of a triblock copolymer A-B-B'-A' and a diblock copolymer B'-A', wherein the molar weight ratio B'/B'B depends on the moment of the introduction of additional initiator. The molar weight ratio B'/B'B is specified in the range of from 0.3 to 0.7, more preferably from 0.4 to 0.6 and even more preferably from 0.45 to 0.55.

European patent application no. 0 636 654 discloses a colour stable block copolymer composition for hot melt adhesives, comprising linear styrene/isoprene/styrene triblock copolymer and a specific stabiliser set in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of linear block copolymer.

The triblock copolymer is prepared by anionic sequential polymerisation of styrene and isoprene, optionally in combination with a second initiation, to provide additional diblock copolymer in an amount of less than 40 wt%, relative to the total weight of block copolymer.

It will be appreciated that for economic and environmental reasons it would be desirable to be able to provide hot melt adhesive compositions having a low melt viscosity at the processing temperatures of the most relevant applications, that is in the range from 100 to 200 °C.

A low melt viscosity not only reduces the need for organic solvent-based adhesive formulations (compositions) in a number of applications, but also allows for formulation freedom in other applications. For example, in a number of adhesive formulations a plasticiser, typically oil, is added to reduce the

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viscosity thereof. Thus, in such formulations it would be possible to lower the amount of plasticiser whilst maintaining the same melt viscosity.

5 A reduction in the amount of plasticiser, in particular oil, in adhesive formulations would provide a better formulation stability (less oil migration), and better shear properties.

10 It would further be desirable to be able to provide hot melt adhesive compositions which have acceptable adhesive properties on difficult substrates, that is substrates which normally cannot be easily wetted by the said compositions, such as foams and kraft, including recycled kraft. In particular it would be desirable to be able to provide hot melt adhesive
15 compositions for use in packaging tapes, having a low hot melt viscosity and acceptable or even improved adhesive properties.

Surprisingly, block copolymer compositions have now been found which impart improvements in one or more
20 respects in hot melt adhesive compositions. In particular, block copolymer compositions have been found which impart a lower melt viscosity to such adhesive compositions as compared with compositions where only the block copolymer composition is
25 different, whilst having acceptable, preferably improved, adhesive properties on difficult substrates.

Accordingly, the present invention relates to hot melt adhesive compositions, comprising

(a,1) from 75-90 parts by weight of a triblock copolymer
30 $A_1B_1A_2$ where A_1 and A_2 represent predominantly poly(monovinyl aromatic) blocks of the same or different peak molecular weight in the range of from 5,000 to 20,000 g/mol, wherein B_1 represents a predominantly poly(isoprene) block while the
35 average apparent molecular weight of the total triblock copolymer is in the range of from 160,000

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to 250,000 g/mol, and the monovinyl aromatic monomer content is in the range of from 10 to 30 wt%, preferably from 15 to 25%wt.

- 5 (a,2) from 10 to 25 parts by weight of a diblock copolymer A_3B_2 , wherein A_3 represents a predominantly poly(monovinyl aromatic) block having a peak molecular weight in the range of from 5,000 to 20,000 g/mol, and wherein B_2 represents a poly(isoprene) block having an
- 10 average apparent molecular weight calculated from GPC measurements which is from 80 to 110 %, preferably from 80 to 100% more preferably from 80 to 95%, of the average apparent molecular weight, calculated from GPC measurements, of the block B_1 ,
- 15 and wherein the monovinyl aromatic monomer content is in the range of from 5 to 17%, preferably from 8 to 13%.
- (b) from 50 to 400 parts by weight of a tackifying resin, preferably from 100 to 200 parts by weight.
- 20 (c) from 0 to 100 parts by weight of a plasticiser and/or softening agent, preferably from 0 to 50 parts by weight.

Preferably, blocks A_2 and A_3 have substantially the same molecular weight, more preferably, blocks A_1 , A_2 and A_3 have substantially the same molecular weight.

25

It will be appreciated that another aspect of the present invention is formed by block copolymer compositions, comprising the hereinbefore specified components (a,1) and (a,2), optionally mixed with a stabiliser.

30

The block copolymer composition, comprising the components (a,1) and (a,2) may be stabilised by means of an amount of from 0.1 to 5 parts by weight and preferably from 0.2 to 1 parts by weight of a stabiliser per 100 parts by weight of (a,1) and (a,2).

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The stabiliser (antioxidant), used in accordance with the practice of the present invention includes high molecular weight hindered phenol derivatives, high molecular weight hindered amine or triazine derivatives or phosphorous and/or sulphur-containing hindered compounds, or mixtures thereof.

Examples of suitable stabilizers are those disclosed in European patent specification No. 0659787.

Preferred representatives of stabilizers are pentaerythrityl-tetrakis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamate) (IRGANOX 1010); octadecyl ester of 3,5-bis(1,1-di-methylethyl)-4-hydroxy benzene propanoic acid (IRGANOX 1076); 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine (IRGANOX 565); 2-tert-butyl-6-(3-tert-butyl-2'-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (SUMILIZER GM); tris(nonylphenyl)phosphite; tris(mixed mono- and di-phenyl)-phosphite; bis(2,4-di-tert-butylphenyl)-pentaerythritol diphosphite (ULTRANOX 626); distearyl pentaerythritol diphosphite (WESTON 618); styrenated diphenylamine (NAUGARD 445); N-1,3-dimethylbutyl-N'-phenyl-paraphenylenediamine (SUMILIZER 116 PPD); tris(2,4-di-tert-butylphenyl)phosphite (IRGAFOS 168); 4,4-butyldiene-bis-(3-methyl-6-tert-butylphenol) (SUMILIZER BBMS); or combinations thereof.

Most preferably are used combinations of tris(nonylphenyl)phosphite (TNPP) and IRGANOX 1076, IRGANOX 565, IRGANOX 1010 or SUMILIZER GM. (IRGANOX, SUMILIZER, ULTRANOX, NAUGARD, WESTON and IRGAFOS are trade marks.)

The content of monovinyl aromatic monomer in the triblock copolymer is preferably from 15 to 25% by weight, more preferably from 15 to 20% by weight. In the triblock and diblock copolymers, the polymerised monovinyl aromatic blocks are preferably polymerised styrene blocks.

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The predominantly poly(isoprene) blocks of the triblock copolymers to be used in the adhesive compositions according to the present invention typically have average apparent molecular weights, calculated from GPC measurement of the initial prepared poly(monovinyl aromatic) blocks, the final diblock copolymer and the final complete triblock copolymer, in the range of from 80,000 to 250,000, preferably from 100,000 to 240,000, and more preferably in the range of from 100,000 to 200,000 g/mol.

It has now been found that the length of the predominantly, poly(monovinyl-aromatic) blocks has a significant influence on the Hot Melt Viscosity of the hot melt adhesive compositions according to the invention. Therefore, the predominantly poly (monovinylaromatic) blocks preferably have a peak molecular weight ranging from 9,000 to 15,000 g/mol, more preferably from 9,000 to 11,000 g/mol.

Also, the average apparent molecular weight of the total triblock copolymer has an influence on the Hot Melt Viscosity of the hot melt adhesive compositions according to the invention. Preferably, the average apparent molecular weight of the triblock copolymer is less than 230,000 g/mol, more preferably from 170,000 to 220,000 g/mol, even more preferably from 180,000 to 205,000 g/mol.

Thus, if one wants to improve existing commercially available block copolymer compositions for use in hot melt adhesive compositions, the said block copolymer compositions having a polyisoprene block in the diblock copolymer having an apparent average molecular weight which is less than 80% of the average apparent molecular weight of the polyisoprene block in the triblock copolymer, whilst retaining the same total polystyrene content, it is preferred to reduce the

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length of the polyisoprene block in the triblock copolymer.

With the term "predominantly poly(monovinyl aromatic", as used throughout the specification, is meant poly(monovinyl aromatic) homopolymer blocks e.g. pure poly(styrene); copolymer blocks derived from a monovinyl aromatic monomer such as styrene, and structurally related monomers e.g. a mixture of a major part of styrene and a minor part (<20 wt%) of an alkyl-substituted styrene, the alkyl substituent(s) containing from 1 to 4 carbon atoms, e.g. α -methylstyrene, o-methylstyrene, p-methylstyrene, p-tert.butyl styrene; 1,3-dimethylstyrene or mixtures thereof); or copolymer blocks derived from a monovinyl aromatic monomer and structurally not related comonomers, such as styrene in a major amount and isoprene in a minor amount (<15 wt%).

With the term "predominantly poly(isoprene)", as used throughout the specification, is meant poly(isoprene) homopolymer blocks; blocks of isoprene and structurally related comonomers having from 2 to 6 carbon atoms, such as butadiene; blocks of isoprene and structurally not related comonomers, typically monovinyl aromatic monomers; or combinations thereof.

Structurally related co-monomers typically may be present in an amount of up to 20% by weight of the polymer block, preferably not more than 10% by weight.

Structurally not related comonomers typically may be present in an amount of up to 15% by weight of the polymer block, preferably not more than 10% by weight, more preferably not more than 5% by weight.

The predominantly poly(isoprene) blocks can be derived from substantially pure isoprene feedstock as well as from lower concentrate isoprene feedstocks (>50 wt% isoprene) containing inert C₅ paraffins and mono-olefins. The term inert means that in the

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isoprene containing mixture, polymerisation killers have been inactivated e.g. by treatment with finely divided sodium in oil.

5 Preferably block copolymers, containing substantially pure poly(styrene) and substantially pure poly(isoprene) are used in the hereinbefore defined hot melt adhesive compositions.

10 With the term "apparent molecular weight" as used throughout this specification, the molecular weight of a polymer is meant, except polystyrene itself, as measured with gel permeation chromatography (GPC) using polystyrene calibration standards as described in ASTM D 3016.

15 With the term "peak molecular weight" is meant the molecular weight corresponding to the peak in the Gel Permeation Chromatogram. For monodisperse polystyrene blocks, the peak molecular weight corresponds, substantially to the true molecular weight.

20 The average apparent molecular weight of the respective poly(isoprene) blocks can be calculated from the apparent molecular weights measured for the respective diblock and triblock copolymers and the initially prepared living poly(styrene) blocks.

25 It will be appreciated that the finally used block copolymers are consisting of mixtures of triblock copolymers $A_1B_1A_2$ and a predetermined well adjusted amount of corresponding diblock copolymers A_3B_2 . Such mixtures of block copolymers are obtainable by a polymerisation process as specified in US patent no.
30 5,405,903, or by mixing in such a predetermined well adjusted amount of diblock copolymer (A_3B_2) into the triblock copolymer before or after termination and/or recovery.

35 Examples of tackifying resins useful in the compositions of this invention include hydrocarbon resins, synthetic polyterpenes, rosin esters and

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natural terpenes which are semi-solid or solid at ambient temperatures, and soften or become liquid, that is, have a ring and ball softening point (ASTM E 28-58T), at temperatures typically ranging from 70°C to 150°C, preferably from 85°C to 120°C. Such tackifying resins are often referred to as primary tackifying resins.

Exemplary of the primary tackifying resins are compatible resins such as (1) natural and modified rosins such as gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerised rosin; (2) glycerol and pentaerythritol esters of natural and modified rosins such as, for example, the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerised rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; (3) copolymer and terpolymers of natured terpenes, e.g., styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins the latter polyterpene resins generally resulting from the polymerisation of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such as, for example, the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins; the latter resins resulting from the polymerisation of monomers consisting primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins (7). Mixed aromatic and aliphatic paraffin hydrocarbon resins, and the hydrogenated derivatives thereof; (8)

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aromatic modified alicyclic petroleum resins and the hydrogenated derivatives thereof; and (9) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. The preferred primary tackifying resins for use in the practice of this invention are represented by sub-paragraphs (1), (6), (7), (8) and (9), supra.

Various plasticising and/or softening agents are useful in the practice of this invention. The plasticiser and/or softening agent can be used to reduce viscosity and/or improve tack properties respectively.

Softening agents which have been found useful include olefin oligomers and secondary tackifying resins. The oligomers may be polypropylenes, polybutenes, hydrogenated polyisoprene, hydrogenated polybutadiene, polypiperylene and copolymers of piperylene and isoprene, or the like having average molecular weights between 350 and 35,000.

Secondary tackifying resins are liquid at ambient temperature, that is 50°C or less. Suitable secondary tackifying resins are typically selected from the same classes (1) to (9) of primary tackifying resins, supra. Preferably, the secondary tackifying resin is selected from the class (1), (6), (7), (8) and (9), supra.

Examples of suitable plasticisers include petroleum-derived oils, synthetic oils such as oils prepared by a Fischer-Tropsch synthesis, as well as vegetable and animal oil and their derivatives.

The petroleum derived oils which may be employed are relatively high boiling materials containing only a minor proportion of aromatic hydrocarbons (preferably less than 30% and, more particularly, less than 15% by weight of the oil). Alternately, the oil may be totally non-aromatic.

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Vegetable and animal oils include glyceryl esters of fatty acids and polymerisation products thereof.

If desired, a filler may also be present in the hot melt adhesive composition in an amount from 0 to 50 parts by weight. Examples of suitable fillers include refractory oxides and carbonates.

According to a preferred embodiment of the present invention, the block copolymer constituents are prepared by sequential polymerisation, in combination with reinitiation, using sec-butyllithium or n-butyllithium as initiator for both initiations in a solvent comprising cyclopentane or cyclohexane, termination of the living polymer(s) with water, alcohol, hydrogen, mono epoxy compounds and preferably alcohols and more preferably methanol, followed by recovery of the block copolymer(s) by hot water and/or steam coagulation and dewatering and/or drying.

The stabiliser can be added after termination of living polymer or at any later stage of the manufacturing process, but preferably just after termination.

The solvent to be used for the preparation of the block copolymer(s), is preferably substantially pure cyclohexane or substantially pure cyclopentane, or mixtures of one of these solvents as main solvent with a minor amount (<50 wt%) of linear or branched alkanes having 5 to 7 carbon atoms such as n-hexane, isopentane or n-pentane. Very suitable are cyclohexane, cyclohexane/n-hexane mixtures, cyclohexane/isopentane/n-hexane mixtures, cyclopentane and cyclopentane/isopentane mixtures. Cyclohexane/isopentane mixtures, substantially pure cyclohexane or cyclopentane are particularly preferred and cyclopentane is the most preferred.

It will be appreciated that an unexpected advantage of the hot melt adhesive compositions is a combination

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of a low melt viscosity at the processing temperatures, enabling said compositions to penetrate sufficiently into the pores of e.g. a foam substrate or kraft, including recycled kraft and acceptable adhesive properties meeting the modern requirements.

A low hot melt viscosity allows industrial processing at higher production speeds. Moreover, a low hot melt viscosity creates formulation freedom as set out hereinbefore, and allows industrial processing at lower temperatures.

The invention is further illustrated by the following examples without, however, restricting the scope of the invention to these examples.

From the polystyrene content and the molecular weight of the block copolymers as determined by Gel Permeation Chromatography (GPC) other data such as the molar weight ratio of the respective polyisoprene blocks in the triblock and diblock copolymers and the styrene weight ratio triblock/diblock can be derived.

Examples

Hot melt adhesive formulations were prepared from two styrene-isoprene-styrene block copolymer compositions according to the present invention (A and B) and from a prior art block copolymer, earlier proposed for similar purposes, (KRATON D 1161 identified by C), as listed in the following tables.

All formulations were compounded in a WERNER and PFLEIDERER Z blade mixer (trademark) at 140°C under nitrogen blanket.

Two lines of hot melt were applied with a MELTEX (trademark) hot melt gun at 160°C onto 2.54 cm (one inch) wide substrates. The coated part was laminated with a second substrate layer by means of a standardised roller. The lamination took place immediately after applying the hot melt (warm).

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A T-peel test was used to assess the adhesion/cohesion of the samples. All adhesive compositions were tested on polyether foam and Kraft (warm and cold).

5 The hot melt adhesive composition comprising C was compared with that one comprising block copolymer B on polyethylene security envelopes. In this application, the adhesive composition should not peel off easily when opening the envelope. The plastic must be damaged
10 which will indicate that the envelope has been opened.

 An acryl modified polyurethane foam was used to compare adhesive compositions comprising the block copolymers B and C. These kind of foams are difficult to adhere on because the acryl modifier is a release
15 agent.

 For this test, a 6 cm sample (2.54 cm wide) was coated over its first 3 cm with two lines of the hot melt adhesive, the sample was folded over 180°C and the coated part was stuck to the non-coated part. A two
20 kilogram weight was put on the folded sample for 1 hour. The two parts were separated by hand in order to assess the difference between the respective samples.

 As is apparent from Table II, the Hot Melt Viscosity of composition A is significantly lower than the Hot Melt Viscosity of composition C. The Hot Melt
25 Viscosity of composition B was 266 Pa.s, which was attributed to the high Mw of the styrene blocks in the block copolymer composition as compared with compositions A and C.

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Table I

SIS block copolymer	A	B	C
MW after first polymer step (kg/mol)	10.6	11.7	10.9
MW of complete block copolymer (kg/mol)	192.7	214.6	210
MW block B ₁ (kg/mol)	172.7	191.2	188.2
% diblock	17	17	17
PSC (%) (ex NMR)	15	15	15
% Mw block B ₂ rel. to block B ₁	100	100	50
Tg	-65	-65	-65
MFR (g/10min 200°C/5 kg)	16	10	11
MFR calc (g/10min 200°C/5 kg)	13	6	11
Hardness Shore A	31	33	30
Solution Viscosity (Pa.s)	0.93	1.48	1.30
Tensile Strength (MPa)	32	32	28
Modulus 300% (MPa)	1.1	1.0	0.6
Modulus 500% (MPa)	1.6	1.5	0.9
Modulus 700% (MPa)	2.3	2.6	1.3
Elongation at break (%)	1200	1100	1300

Table III

	B	C	B	C	B	C
SIS block copolymer	100	100	100	100	100	100
PICCOTAC 95E	-	-	56	56	-	-
SCOREZ 2203	100	100	-	-	-	-
MBG206	-	-	94	94	-	-
FORALYN 110	-	-	-	-	134	134
KRISTALEX 5140	-	-	-	-	25	25
CATENEX N 956	20	20	-	-	40	40
IRGANOX 1010	1	1	1	1	-	-
HP kraft 23°C	78	65	-	-	-	-
Flaptest KRAFT 23°C	62	58	-	-	-	-
PA 90° BOPP	-	-	8	7	-	-
T-peel polyether foam	-	-	-	-	7	5
T-peel kraft	-	-	-	-	5	2
T-peel PE	-	-	-	-	9	2
180° peel PU acryl modified	-	-	-	-	a	b

a: difficult to peel off; b: easy to peel off

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TABLE IV
SPECIFICATION OF AUXILIARIES

ESCOREZ 2203	Slightly aromatic modified hydrocarbon resin. EXXON.
PICCOTAC 95E	Aliphatic C5-hydrocarbon resin. HERCULES.
HERCULES MBG 206	Liquid aliphatic hydrocarbon resin. HERCULES.
FORALYN 110	Hydrogenated resin ester. HERCULES.
KRISTALEX 5140	Aromatic hydrocarbon resin. HERCULES.
NEVCHEM NL140	Alkylaromatic C9 petroleum rosin. NEVCIN.
CATENEX N956	Paraffinic-napthenic oil used as plasticiser. SHELL.
IRGANOX 1010	Pentaerithrytol-tetrakis-[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate]. CIBA-GEIGY.
PICCOTAC 212	low molecular weight aliphatic hydrocarbon resin. HERCULES

TABLE V
ADHESIVE TEST METHODS

5

Property	Test Procedure
Rolling Ball Tack	PSTC 6; ASTM D3121-89
Loop Tack	FTM 9
180° Peel Adhesion	PSTC 1; ASTM D3330M-90
Holding Power 2 kg/23°C	ASTM D-3654M-88; FTM 8
Shear Adhesion Failure Temperature	Method as specified*
Hot-Melt Viscosity at 160°C	ASTM D3236-88
Melt Flow Rate	ISO 1133
Solution Viscosity at 25 %wt.	ASTM D 2857-93
Stress Strain Properties	ASTM 412D
Gel Permeation Chromatography	ASTM D 3016
Flap test Kraft	Method as disclosed in European Adhesives & Sealants, December 1991, pages 21-24
Polystyrene content	ASTM D 3314-92

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* The Shear Adhesion Failure Temperature (SAFT) test is designed to give an indication of the short-term heat resistance under defined conditions, such as loads and temperature increase.

5 The SAFT test is carried out in an air circulating oven equipped with an electro-mechanical device monitoring a stepwise increase of the temperature. Inside the oven, supports are attached to the side walls on which six aluminium racks can be placed under
10 an angle of 2°. These racks support 6 metal or glass plates onto which the tape samples will be applied. These plates rest against a narrow ridge in which 6
15 slots are cut; the free part of the coated film on which the weights are hung, passes along these slots.

15 One end of the strip is centred and stuck partially onto a glass plate; the other end of the strip is held so that it does not make contact with the plate but is positioned below. The strip is pressed firmly against the glass plate avoiding entrapment of air bubbles.
20 The adhered part of the strip is cut at 1" of the glass edge. The surface is then 25.4 mm x 25.4 mm (1 inch²). Finally, the test specimens are stored for 24 hours.

 The racks with the samples are installed in the oven and weights of 500 or 1000 grams are hung to the
25 free end of the strip and clamped with "Hofmann" hose clamps.

 These weights are initially supported by a base plate which can move up and downwards by means of a "lab jack". Just before the start of the test, the
30 base plate is moved downwards so that the weights now hang freely above the micro or photo-electrical switches. These switches are connected to a counter. The temperature in the oven is displayed on a digital thermometer.

35 When a strip falls, the weight falls down on the micro switch and the timer is stopped. When the time

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to failure is known, the temperature at which failure occurred can be read off from the calculated time/temperature diagram. The SAFT value is the average of two temperatures recorded with two samples.

5 Further hot melt adhesive formulations for use in packaging tapes were prepared as described herein before, from one styrene-isoprene-styrene block copolymer composition according to the invention (D) and, for comparison, two styrene-isoprene-styrene block
10 copolymer compositions not according to the invention (E and F), as listed in the following tables. The polyisoprene block of the diblock copolymer of composition F had an average apparent molecular weight of less than 80%, whereas in composition E the diblock
15 content was greater than 25 parts by weight. Block copolymer composition F is a sample of the same grade as composition C.

As can be seen from Table VII, packaging tape formulations prepared from block copolymer compositions
20 according to the invention not only have a low Hot Melt Viscosity (HMV), but also sufficient adhesive properties.

As discussed herein before, the low Hot Melt Viscosity leaves scope for even improving upon the
25 adhesive properties of the formulation. It belongs to the skill of the skilled adhesive formulator to select appropriate formulations for improving adhesive properties whilst somewhat increasing the Hot Melt Viscosity. Preferably, the Hot Melt Viscosity in
30 adhesive formulations is not more than 80 Pa.s at 190 °C, as most existing industrial facilities will have difficulty dealing with higher Hot Melt Viscosities.

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Table VI

SIS block copolymer	D	E	F
MW after first polymer step (kg/mol)	10.6	10.8	10.8
MW of complete block copolymer (kg/mol)	183	174	215
MW block B ₁ (kg/mol)	154.7	162.6	193.4
% diblock	17	28	18
PSC (%) (ex NMR)	15	15	15
% MW block B ₂ rel. to block B ₁	100	100	50
MFR (g/10min 200°C/5 kg)	15	26	11
Solution Viscosity (Pa.s)	0.9	0.8	1.3
Tensile Strength (MPa)	25	14	28
Modulus 300% (MPa)	0.9	0.9	0.6
Modulus 500% (MPa)	1.4	1.2	0.9
Modulus 700% (MPa)	2.2	1.8	1.3
Elongation at break (%)	1200	1200	1300

Table VII

		D	E	F
SIS block copolymer	parts	100	100	100
PICCOTAC 212	phr	100	100	100
IRGANOX 1010	phr	2	2	2
HMV 190°C	Pa.s	57.6	55.2	107
HP kraft 40°C	hrs	19	1	17
Flaptest KRAFT 23°C	hrs	45	23	67

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C L A I M S

1. Hot melt adhesive compositions comprising:

(a,1) from 75-90 parts by weight of a triblock copolymer $A_1B_1A_2$ where A_1 and A_2 represent predominantly poly(monovinyl aromatic) blocks of the same or different peak molecular weight in the range of from 5,000 to 20,000 g/mol, wherein B_1 represents a predominantly poly(isoprene) block while the average apparent molecular weight of the total triblock copolymer is in the range of from 160,000 to 250,000 g/mol, and the monovinyl aromatic monomer content is in the range of from 10 to 30 wt%,

(a,2) from 10 to 25 parts by weight of a diblock copolymer A_3B_2 , wherein A_3 represents a predominantly poly(monovinyl aromatic) block having a peak molecular weight in the range of from 5,000 to 20,000 g/mol, and wherein B_2 represents a poly(isoprene) block having an average apparent molecular weight calculated from GPC measurements which is from 80 to 110% of the apparent average molecular weight calculated from GPC measurements of block B_1 , and wherein the monovinyl aromatic monomer content is in the range of from 5 to 17%.

(b) from 50 to 400 parts by weight of a tackifying resin.

(c) from 0 to 100 parts by weight of a plasticiser and/or softening agent.

2. Hot melt adhesive composition according to claim 1, characterised in that the components (a,1) and (a,2) have been stabilised by means of a stabiliser in an

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amount from 0.2 to 1 parts by weight per 100 parts by weight of (a,1) and (a,2).

3. Hot melt adhesive composition according to claims 1 or 2, characterised in that the predominantly poly(isoprene) blocks of the triblock copolymers have average apparent molecular weights in the range of from 100,000 to 240,000 g/mol, calculated from GPC measurements of the initial prepared homopoly(monovinylaromatic) block, the final diblock copolymer and the triblock copolymer.
4. Hot melt adhesive composition according to claims 1-3, characterised in that the peak molecular weight of the predominantly poly(monovinylaromatic) blocks is in the range of from 9,000 to 15,000 g/mol.
5. Hot melt adhesive composition according to claims 1-4, characterised in that the tackifying resins include hydrocarbon resins, synthetic polyterpenes, rosin esters and natural terpenes, which are semi solid or solid at ambient temperatures, and have a ring and ball softening point (ASTM E28 58T) at a temperature ranging from 70°C to 150°C.
6. Block copolymer composition, comprising:
(a,1) from 75-90 parts by weight of a triblock copolymer $A_1B_1A_2$ where A_1 and A_2 represent predominantly poly(monovinyl aromatic) blocks of the same or different peak molecular weight in the range of from 5,000 to 20,000 g/mol, wherein B_1 represents a predominantly poly(isoprene) block while the average apparent molecular weight of the total triblock copolymer is in the range of from 160,000 to 250,000 g/mol, and the monovinyl aromatic monomer content is in the range of from 10 to 30 wt%,
(a,2) from 10 to 25 parts by weight of a diblock copolymer A_3B_2 , wherein A_3 represents a predominantly poly(monovinyl aromatic) block

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5 having a peak molecular weight in the range of
from 5,000 to 20,000 g/mol, and wherein B₂
represents a poly(isoprene) block having an
average molecular weight calculated from GPC
measurements which is from 80 to 110% of the
average molecular weight calculated from GPC
measurements of block B₁, and wherein the
monovinyl aromatic monomer content is in the range
of from 5 to 17%.

10 7. Block copolymer composition according to claim 6
characterised in that the components (a,1) and (a,2)
have been stabilised by means of a stabiliser in an
amount from 0.2 to 1 parts by weight per 100 parts by
weight of (a,1) and (a,2).

15 8. Block copolymer composition according to claims 6
or 7 characterised in that the predominantly
poly(isoprene) blocks of the triblock copolymers have
average apparent molecular weights in the range of from
100,000 to 240,000 g/mol, calculated from GPC
20 measurements of the initial prepared
homopoly(monovinylaromatic) block, the final diblock
copolymer and the triblock copolymer.

25 9. Block copolymer composition according to claims 6-
8, characterised in that the peak molecular weight of
the predominantly poly(monovinylaromatic) blocks is in
the range of from 9,000 to 15,000 g/mol.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01906

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09J153/02 C08L53/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09J C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 16755 A (EXXON CHEMICAL PATENTS INC.) 22 June 1995 see the whole document ---	1,6
A	FR 2 352 045 A (JOHNSON & JOHNSON) 16 December 1977 ---	1
A,P	US H001622 H (G. HIMES) 3 December 1996 see the whole document ---	1,6
A	US 5 405 903 A (J. VAN WESTRENNEN ET AL.) 11 April 1995 cited in the application ---	1
A	US 5 089 550 A (T. SAKAGAMI ET AL.) 18 February 1992 cited in the application ---	1
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 11 July 1997	Date of mailing of the international search report - 4. 08. 97	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Glikman, J-F	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01906

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 636 654 A (SHELL INTERNATIONALE R. M. B. V.) 1 February 1995 cited in the application -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/01906

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9516755 A	22-06-95	CN 1141644 A EP 0734426 A	29-01-97 02-10-96
FR 2352045 A	16-12-77	US 4080348 A AU 512345 B AU 2478377 A CA 1087341 A GB 1558220 A IN 146069 A JP 1554888 C JP 52140544 A JP 61006872 B	21-03-78 09-10-80 09-11-78 07-10-80 19-12-79 17-02-79 23-04-90 24-11-77 01-03-86
US H001622 H	03-12-96	NONE	
US 5405903 A	11-04-95	BR 9405911 A CN 1120342 A WO 9422931 A EP 0691991 A JP 8508309 T	26-12-95 10-04-96 13-10-94 17-01-96 03-09-96
US 5089550 A	18-02-92	CA 1326087 A EP 0330764 A JP 7055999 B JP 63066254 A AU 612142 B AU 1484988 A WO 8908128 A	11-01-94 06-09-89 14-06-95 24-03-88 04-07-91 22-09-89 08-09-89
EP 636654 A	01-02-95	BR 9402946 A JP 7062198 A	11-04-95 07-03-95