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(54) **Title**: CAUSTIC REMOVABLE HOT MELT ADHESIVE FORMULATIONS

(57) **Abstract**: The invention relates firstly to a hot melt adhesive additive, particularly comprising a low molecular weight styrene-maleic anhydride (SMA) and a low molecular weight maleated polybutadiene imparting caustic removability to a conventional hot melt adhesive composition comprising the said additive. It relates also to a caustic removable hot melt adhesive composition comprising said adhesive additive and further comprising an adhesive resin of the group consisting of styrene-isoprene-styrene block copolymers, tackifying resins, polyacrylate resins, poly ethylene vinyl acetate resins, polystyrene butadiene resins, styrene-butadiene-styrene block copolymers, and process oil, or mixtures thereof. It covers also a caustic removable hot melt adhesive label which comprises said caustic removable hot melt adhesive composition.

CAUSTIC REMOVABLE HOT MELT ADHESIVE FORMULATIONS

This invention relates to hot melt adhesive formulations which have caustic removability properties. More particularly, the invention relates to an additive composition which imparts caustic removability properties to hot melt adhesive formulations. Additionally, this invention relates to the hot melt adhesive composition comprising said additive composition, to adhesive labels and to articles upon which the adhesive label is adhered with the adhesive compositions of the invention.

Hot melt adhesives typically exist as entirely solid materials which do not contain or require any solvents. They are solid materials at ambient room temperature but can be converted to a flowable liquid or fluid state by the application of heat, in which state they may be applied to a substrate. On cooling, the adhesive regains its solid form and gains its cohesive strength. In this regard, hot melt adhesives differ from other types of adhesives, such as water-based adhesives, which achieve the solid state by evaporation, removal of solvents, polymerization, or other means.

These adhesives are particularly useful in the manufacture of a variety of industrial or consumer goods where bonding of various substrates is necessary. An advantage of hot melt adhesives is the absence of a liquid carrier, as would be the case for water-based or solvent-based adhesives, which requires a drying step during application of the adhesive. Suitable hot melt adhesives possess the appropriate bond strength to adhere the substrates involved, and also demonstrate adequate flexibility, no staining or bleed through of the substrate, suitable viscosity and open time to function on a variety of substrates, acceptable stability under storage conditions, and acceptable thermal stability under normal application temperature.

Hot melt adhesives may be formulated to be relatively hard and free of tack or, in contrast, to be pressure sensitive, i.e., relatively soft and tacky at room temperature. Hot melt adhesives are increasingly utilized for affixing labels to various substrates, such as to glass or plastic bottles. Pressure sensitive hot melt adhesives for labeling are usually categorized as either removable or permanent. Permanent adhesives are formulated to cause the label to tear upon removal from

the substrate. On the contrary, removable adhesives must allow the label to be removed from the substrate with a clean release, i.e., leaving no residue and without the tear of the label stock which occurs in a permanent adhesive application.

Solid hot melt adhesives for permanent adhesives have been widely used for many years. However, a hot melt adhesive, and more particularly a hot melt pressure sensitive adhesive, that gives good removability has not been available. Current removal adhesives are supplied for label stock from acrylic lattices and solvented solution adhesives. Both of these materials have high molecular weight polymers that reduce flow on a surface to prevent build up of adhesion. In contrast, hot melt adhesives, in particular hot melt pressure sensitive adhesives, are based on materials having lower molecular weight polymers and high amounts of very low molecular weight components that make reduced flow or wetting on a surface very difficult.

Many different polymers have been used in hot melt adhesives employed in the construction of industrial or consumer goods. Typical hot melt adhesives have employed polymers which have included tri-block copolymers such as styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS), styrene-ethylene-butylene-styrene (SEBS), ethylene-vinyl acetate (EVA) copolymers, and/or amorphous poly-alpha-olefin (APAO). Although these polymers, when properly blended, provide adhesion to most substrates, they are not suitable for certain particular uses. One shortcoming of the prior hot melt adhesives concerns their removability, which is an important feature for purposes of recycling the substrate.

To improve removability of the hot melt adhesive, the prior art has aimed to increase the water-solubility or water-dispersibility characteristics of the adhesive. For example, one known water sensitive hot melt adhesive composition which may be utilized in the manufacturing of disposable goods, especially disposable nonwoven articles, combines high dry bond strength with increased water solubility, thereby permitting the component elements of the disposable article to be recycled or otherwise disposed of in an environmentally friendly manner (i.e., degraded). Other known adhesives relate to a water-soluble or water-dispersible hot melt composition based on graft copolymers. These water-removable hot melt

adhesives are used for labelling returnable bottles at high speeds, wherein the labels can be removed by brief soaking in hot water. However, these water-soluble compositions are not favorably employed to adhere labels to glass bottles, where water-resistant characteristics are desired as much as the clean removability of pressure sensitive labels.

Conventional styrene-isoprene-styrene (SIS) block copolymer/hydrocarbon (HC) tackifier-based hot melt adhesives have been used to adhere labels to glass bottles for decades. One of the beneficial properties of these types of adhesives for this application is that they can withstand a 7-day water immersion test. Accordingly, these types of adhesives are known for their favorable water-resistant characteristics. However, this presents a difficult challenge when the labels and adhesives need to be removed in a glass bottle recycling process. Hot caustic baths are successfully used to remove many water-based label adhesives. However, the hot melt adhesives are very resistant to caustic.

A new additive has now been discovered which imparts caustic removability to conventional hot melt adhesives. For example, particular additives of the present invention impart caustic removability to styrene-isoprene-styrene (SIS) block copolymer/hydrocarbon (HC) tackifier-based hot melt adhesives. An adhesive containing the additive may be formulated to achieve similar water resistance and adhesive strength properties as when the additive is not present, while enabling the clean removability of the labels in caustic baths for recycling purposes. The adhesive containing the additive may be applied to a substrate, such as paper for an adhesive label for adhesion to an article, such as a glass bottle or container. The presence of such an additive in a hot melt adhesive composition does significantly improve the caustic removability of said adhesive while keeping unaffected its essential viscoelastic performances, with still good enough adhesive properties.

A first subject of the present invention relates to an adhesive additive composition, for imparting caustic removability to a hot melt adhesive.

A second subject of the invention relates to a hot melt, particularly hot melt pressure sensitive adhesive composition, comprising the said adhesive additive composition.

Another subject of the invention relates to a hot melt adhesive label, which comprises the said hot melt adhesive composition, removable by caustic solution.

The uses of both, the said additive composition but also of the said hot melt adhesive composition, in caustic removable adhesives or adhesive labels, are equally covered by the present invention.

Finally the present invention does also cover an article, comprising an adhesive label as defined according to the invention, adhered to, more particularly with said article being recyclable.

A first subject of the present invention relates to an additive composition for imparting caustic removability to a hot melt adhesive, which additive composition comprises at least one low molecular weight polymer or resin, with both terms "polymer" or "resin" being used in the present invention with the same meaning, the said polymer containing, in its composition, one or more α,β ethylenically unsaturated carboxylic anhydride or acid. More particularly, the said low molecular weight α,β ethylenically unsaturated carboxylic anhydride-containing or acid-containing polymer (or resin) is selected from the group consisting of : low molecular weight copolymers or homopolymers, preferably copolymers and more preferably their partial esters, of the said unsaturated anhydride or acid and/or low molecular weight polymers chemically grafted with the said anhydride or acid. Combination of at least two of these polymers is possible and is even preferred and it is even more preferred a combination of a) at least one of said copolymers, preferably one of said esters of copolymers, and of b) at least one of said grafted polymers as defined above.

The meaning of the term "low molecular weight", as defined above, does mean a weight average molecular weight Mw of less than 50000 (by GPC with polystyrene standards in THF). The said anhydride or acid may be selected from maleic anhydride, fumaric acid, itaconic anhydride or acid and tetrahydrophthalic anhydride or acid. Preferably, it is maleic anhydride or fumaric acid and more preferably maleic anhydride. The said copolymers of the said unsaturated anhydride or acid may be copolymers of said anhydride or acid with a comonomer selected from vinyl aromatic monomers like vinyl toluenes and styrene or from ethylene and/or propylene. Preferable molar ratio of the said comonomer to the

said anhydride or acid ranges from 1/1 to 2/1. A particular case of such a copolymer of said anhydride or acid is a copolymer of maleic anhydride or fumaric acid with at least one monomer selected from vinyl aromatic monomers or from ethylene and/or propylene. A more preferred copolymer is a maleic anhydride-styrene copolymer, particularly with a molar ratio S/MA of styrene (S) to maleic anhydride (MA) ranging from 1/1 to 2/1, more preferably 1.4/1 to 1.6/1. These copolymers are preferably at least partially esterified copolymers, which are esterified by a monoalcohol which may be a C1 to C12 linear or branched monoalcohol (if branched in C4 to C12) preferably from C2 to C8 (if branched from C4 to C8). "Esterified" in the case of these copolymers, means having a monoesterified anhydride or acid, corresponding to one carboxy group from two being esterified when fully (100%) esterified.

The polymers of the said chemically grafted polymers of said additive composition, may be selected from diene homopolymers and/or from diene copolymers or from homopolymers and/or copolymers of ethylene and/or propylene, and/or from tackifying resins preferably tackifying resins from C5 and/or C9 hydrocarbon resins or rosin esters. The corresponding grafted polymers may have a weight content of said unsaturated anhydride or acid ranging from 10 to 50% and preferably from 10 to 30%. The preferred anhydride or acid for these grafted polymers is maleic anhydride or fumaric acid and more preferably maleic anhydride, which means that these polymers are maleated (maleic-grafted) polymers. Even more preferably, this grafted polymer is a maleated diene homopolymer or copolymer, the said diene being butadiene and/or isoprene. Suitable diene copolymers for these grafted polymers are copolymers of said diene as defined above with vinyl aromatic comonomers, preferably styrene.

In at least one more specific embodiment, the additive composition of the present invention comprises at least two low molecular weight α,β ethylenically unsaturated carboxylic anhydride- or acid-containing polymers as defined above. Preferably, the said additive composition comprises at least the following two polymers (or resins) a) and b) :

a) at least one low molecular weight partial ester of a copolymer of said unsaturated anhydride or acid, preferably the said copolymer being a

maleic anhydride-vinyl aromatic monomer copolymer and more preferably being a styrene-maleic anhydride copolymer as defined above according to the invention.

b) at least one low molecular weight polymer grafted by said unsaturated anhydride or acid, preferably the said grafted polymer being a maleated diene homopolymer or copolymer, more preferably being a maleated polybutadiene, as defined above according to the invention.

It is possible that the said unsaturated anhydride or acid in said polymers or resins a) and b) as defined above, is the same or different, preferably being the same anhydride or acid.

More preferably, the said additive is a combination or mixture of a low molecular weight maleic anhydride-vinyl aromatic monomer copolymer preferably its partial ester, such as a partial ester of low molecular weight styrene-maleic anhydride (SMA) copolymer, and a low molecular weight maleic anhydride grafted polymer, such as a low molecular weight maleated polydiene, such as maleated polybutadiene and/or polyisoprene, preferably maleated polybutadiene. The additive combination of a) a low molecular weight styrene-maleic anhydride ester and b) a maleated polybutadiene resin imparts caustic removal properties to a conventional hot melt adhesive formulation. Adhesives formulated with this combination additive can be used in hot melt adhesive labels, particularly in hot melt pressure sensitive labels for recyclable glass articles, such as bottles. The labels can be removed with caustic, such as in a hot caustic bath, when the objects are recycled. Without being held to the theory, it is believed that the acid and/or anhydride groups of the additive components impart caustic solubility to the otherwise insoluble current hot melt adhesive components among : block copolymer, such as styrene-isoprene-styrene block copolymer, tackifying resins such as hydrocarbon resins, and process oil, such as mineral oil. The desired adhesive properties of the hot melt adhesive are retained even though the caustic removability property has been imparted (improved) by the addition of the said additive.

The second and main subject of the invention is a hot melt adhesive composition, more particularly a hot melt pressure sensitive adhesive composition,

comprising the said additive composition as defined above, as an adhesive additive component of the said hot melt composition. The hot melt adhesive composition of the invention is caustic removable and it comprises the said adhesive additive which comprises at least one, preferably at least two, low molecular weight polymer (or resin), which polymer (or resin) contains in its composition, at least one α,β ethylenically unsaturated carboxylic anhydride or acid, the said polymer being selected from : low molecular weight copolymers of the said unsaturated anhydride or acid, preferably their partial esters, and/or low molecular weight polymers chemically grafted with the said anhydride or acid. Combination of at least two of these polymers is possible and even preferred and even more preferred is a combination or mixture of : a) at least one of said copolymers and of b) at least one of said grafted polymers as defined above.

More particularly, the said hot melt adhesive composition comprises in addition to the said additive, an adhesive resin of the group consisting of styrene-isoprene-styrene (SIS) block copolymers, hydrocarbon or rosin ester tackifying resins, polyacrylate resins, poly ethylene vinyl acetate (EVA) resins, polystyrene butadiene resins, random styrene-butadiene (SBR) copolymers, styrene-butadiene-styrene (SBS) block copolymers, styrene-ethylene-butylene-styrene (SEBS) block copolymers, amorphous poly-α olefin (APAO) resins, and optionally a process oil, or mixtures thereof. The additive of the hot melt adhesive composition is a low molecular weight α,β ethylenically unsaturated anhydride- or acid-containing polymer, which may be selected from the group consisting of a low molecular weight said unsaturated carboxylic anhydride homopolymer, a low molecular weight said unsaturated carboxylic anhydride- or acid-modified polyolefin; a low molecular weight said carboxylic anhydride or acid-vinyl aromatic copolymer, and a low molecular weight said carboxylic anhydride grafted polymer, or the combination or mixtures thereof. The said unsaturated carboxylic anhydride or acid may be selected from the group consisting of maleic anhydride, fumaric acid, itaconic anhydride or acid, and tetrahydrophthalic anhydride or acid. The preferred from said anhydrides or acids, is maleic anhydride or fumaric acid and even more preferred maleic anhydride. In at least one embodiment, the caustic removable hot melt adhesive composition comprises a) at least one low molecular weight partial

ester of a copolymer of said unsaturated anhydride or acid preferably copolymer with a vinyl aromatic monomer, more preferably styrene-maleic anhydride (SMA) copolymer and b) at least one low molecular weight polymer grafted with said anhydride or acid, preferably polydiene (diene homo- or co- polymer) grafted with said anhydride or acid and more preferably, maleated polybutadiene, at a ratio a):b) of between 60:40 and 40:60. The present invention has a particular usefulness for labels on products which are to be recycled.

In yet another embodiment, the present invention is a caustic removable adhesive label comprising a substrate and a caustic removable hot melt adhesive composition as defined according to the present invention, wherein the said adhesive composition is applied to the substrate for adhesion to a product (article). The label of the present invention may be a label which, after application of the caustic removable hot melt adhesive composition, may be adhered to a product (article) such as a glass bottle. In at least one embodiment, the caustic removable adhesive label contains a hot melt adhesive composition, with said adhesive additive comprising a combination or mixture of a low molecular weight partial ester of a styrene-maleic anhydride (SMA) copolymer or resin and a low molecular weight maleated polybutadiene, in which the low molecular weight SMA ester resin has a ratio of styrene (S) : maleic anhydride (MA) of about 1:1 to about 2:1. The said adhesive additive is soluble in a caustic (basic) solution having a pH greater than 8.

In another embodiment, the present invention is a caustic removable adhesive label and an article having said caustic removable adhesive label adhered to. Particularly, the said article is a container and a caustic removable adhesive label is adhered thereto. The label comprises a substrate, such as paper, and a caustic removable hot melt adhesive composition having an additive as defined above according to the invention, which comprises at least one low molecular weight polymer containing α,β ethylenically unsaturated anhydride or acid as defined above. The said additive is soluble in a caustic solution having a pH greater than 8. The container is made from a material from the group consisting of glass, stainless steel, and high density polyethylene. The label adheres to the article with good adhesion properties, and the article and label are water resistant. The label becomes removable from the article upon being submerged in, or otherwise treated

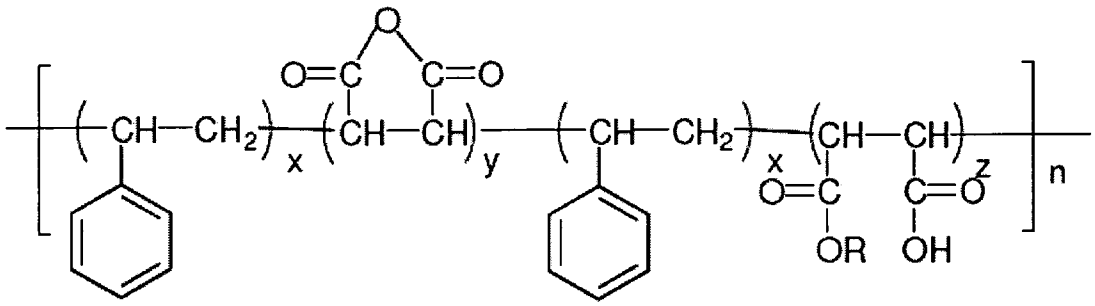
with, a caustic bath having a pH greater than 8.

In a further embodiment of the present invention, the low molecular weight α,β ethylenically unsaturated carboxylic anhydride- or acid-containing polymer is selected from the group consisting of a low molecular weight carboxylic anhydride polymer, a low molecular weight carboxylic anhydride polyolefin, a low molecular weight carboxylic anhydride vinyl aromatic copolymer, and a low molecular weight carboxylic anhydride grafted copolymer, or the combinations thereof ; wherein the carboxylic anhydride or acid is selected from the group consisting of maleic anhydride, fumaric acid, itaconic anhydride or acid, and tetrahydrophthalic anhydride or acid. In yet a further embodiment, the low molecular weight α,β ethylenically unsaturated carboxylic anhydride polymer or acid thereof is selected from the group consisting of a low molecular weight maleic anhydride homopolymer or copolymer, a low molecular weight maleic anhydride polyolefin ; a low molecular weight maleic anhydride vinyl aromatic copolymer, and a low molecular weight maleic anhydride grafted copolymer, or the combinations thereof.

In one embodiment of the present invention, the said adhesive additive is a combination of a) at least one low molecular weight partial ester of an α, β ethylenically unsaturated carboxylic anhydride or acid-vinyl aromatic monomer copolymer and of b) at least one low molecular weight α, β ethylenically unsaturated carboxylic anhydride or acid grafted polymer. The carboxylic anhydride vinyl aromatic copolymer is partially esterified by an alcohol, more particularly by a monoalcohol. For example, the said carboxylic anhydride-vinyl aromatic monomer copolymer may be at least partially esterified by an aliphatic, linear, or branched C1-C12 (if branched C4-C12) monoalcohol, preferably a C2-C8 (if branched C4-C12) monoalcohol. The degree of monoesterification of the said carboxylic anhydride copolymer may range from 50-100% of the initial anhydrides. Additionally, the carboxylic anhydride or acid- vinyl aromatic copolymer can be any partial monoester of the copolymer which is soluble to any degree in basic pH solutions having a pH greater than 8. Both anhydride (or corresponding acid) and ester groups may be present in the carboxylic anhydride or acid-vinyl aromatic monomer copolymer. In at least one embodiment, the carboxylic anhydride-vinyl aromatic copolymer is a styrene maleic anhydride ester ("SMA") copolymer or

resin, preferably with S (styrene):MA (maleic anhydride) molar ration ranging from 1:1 to 2:1. In this embodiment of the present invention, the low molecular weight carboxylic anhydride or acid- grafted polymer of the combination additive is a partially maleated polybutadiene polymer. The maleated polybutadiene copolymer has maleic anhydride content from 10% to 50% w/w, more preferably 10% to 30% w/w, and is soluble to any degree in basic pH solutions having a pH greater than 8. In at least one embodiment, the said carboxylic anhydride-grafted polymer is a diene homopolymer or copolymer grafted with maleic anhydride, such as maleated polybutadiene ("PBD").

In an embodiment of the present invention, the additive comprises a combination of a) a low molecular weight styrene maleic anhydride ester resin and b) a low molecular weight maleated polybutadiene resin. When added to a conventional hot melt adhesive, the combination additive imparts caustic removable properties to the conventional hot melt adhesive formulation. The low molecular weight styrene maleic anhydride ("SMA") ester resin can have the structure of Formula (I) :



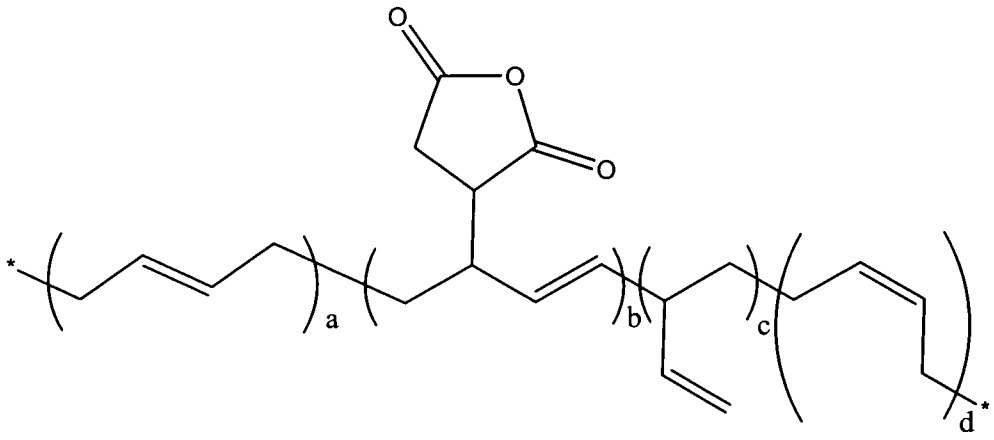
(I)

wherein n, R, x, y, and z are as described below.

The number n of repeating units may be from 7 to 72, preferably 8 to 15 and relates to the molecular weight of this additive component. R can be any residue of an aliphatic, linear, or branched C1-C12 monoalcohol (if branched C4-C12), preferably a C2-C8 (if branched C4-C12) monoalcohol. The monoalcohol may be alkoxylated, such as with up to 8 alkoxy units from an ethoxy group and/or a propoxy group. The SMA ester resin may have different molar ratios of styrene (S) : maleic anhydride (MA) co-monomer compositions, such as a molar ratio x :(y+z) is in the range from about 1:1 to 2:1 and more preferably from about 1.4:1 to 1.6:1. The molecular variables x, y, and z, relate to the molar ratios of S:MA

such that x is from 1 to 4, a molar ratio of (x : (y+z)) is in the range from about 1:1 to 2:1, and the monoesterification molar ratio of (z / (y+z)) ranges from about 50 to 100%. The SMA ester resin can be any partial monoester of a styrene maleic anhydride resin that is soluble to any degree in basic pH solutions having a pH greater than 8. These monoesters have both acid and anhydride functionality. Particular examples of monoalcohols which may comprise R of Formula I include, but are not limited to, isopropyl and cyclohexyl alcohols. For example, the additive composition may be a (45/30) isopropyl/cyclohexyl ester, corresponding to 75% of global monoesterification degree, of a styrene-maleic anhydride (SMA) copolymer and an S:MA ratio of about 1.4:1 to about 1.6:1.

The said low molecular weight maleated polybutadiene ("PBD") can have the structure of Formula (II) :



(II)

with "a" representing trans 1,4 polybutadiene units, "b" maleated polybutadiene units, "c" polybutadiene units with pending vinyl group (1,2 addition) and "d" cis 1,4 polybutadiene units.

The resin of Formula (II) can be any partially maleated polybutadiene resin that is soluble to any degree in basic pH solutions, which means at pH higher than 8. These maleated polybutadiene resins have anhydride functionality. The degree of maleinization (or maleation) of the polybutadiene can range from the least amount needed to render a given polybutadiene partially soluble in a basic pH solution having a pH greater than 8, to as high a level of maleinization as is achievable, while retaining compatibility with the hot melt adhesive formulation components. The maleated polybutadiene copolymer has a maleic anhydride content (i.e., is maleated or maleinized) from 10 to 50% w/w, more preferably 10%

to 30% w/w. In a preferred embodiment of the present invention, the additive composition includes a 20% maleated derivative of a polybutadiene.

The term "low molecular weight" according to the invention generally means a weight average molecular weight Mw less than 50,000 (GPC with polystyrene standards in THF). When a low molecular weight carboxylic anhydride vinyl aromatic copolymer, such as a styrene-maleic anhydride, is used as the additive or as part of a combination additive, the molecular weight may be effected by the degree of monoesterification, among other factors. The molecular weight of the styrene-maleic anhydride copolymer or resin may thus range from 1,000 to 50,000, or more preferably from 2,000 to 15,000. When a low molecular weight carboxylic anhydride grafted copolymer is employed as the additive or as part of a combination additive, such as maleated polybutadiene, the molecular weight may vary depending on the maleic anhydride content (e.g, the degree of maleinization), among other factors. The molecular weight of the maleated polybutadiene may thus be in the range from 1,000 to 25,000, or more preferably from 2,000 to 10,000. When the additive comprises a combination of a low molecular weight styrene-maleic anhydride (SMA) ester resin and a low molecular weight maleated polybutadiene (PBD) resin, the weight ratio of SMA:PBD resins may vary but is preferably from 40:60 to 60:40.

In another embodiment, the present invention is a hot melt adhesive composition which comprises an additive as defined above, that imparts caustic removable properties to a conventional hot melt adhesive composition. The additive comprises at least one, preferably at least two, low molecular weight α,β ethylenically unsaturated carboxylic anhydride or acid-containg polymer as defined above. The low molecular weight α,β ethylenically unsaturated carboxylic anhydride- or acid-containing polymer can be added to any conventional hot melt adhesive formulation, such as comprising an adhesive resin of the group consisting of styrene-isoprene-styrene (SIS) block copolymers, hydrocarbon tackifying resins, polyacrylate resins, poly ethylene vinyl acetate (EVA) resins, polystyrene butadiene resins, random styrene-butadiene (SBR) copolymers, styrene-butadiene-styrene (SBS) block copolymers, styrene-ethylene-butylene-styrene (SEBS) block copolymers, amorphous poly-α olefin (APAO) resins, and a

process oil, or mixtures thereof. The α,β ethylenically unsaturated carboxylic anhydride- or acid-containing polymer, has a molecular weight less than 50,000.

In a further embodiment, the hot melt adhesive composition is formulated with the additive combination of a) a low molecular weight said carboxylic anhydride -vinyl aromatic monomer copolymer and b) a low molecular weight said carboxylic anhydride grafted copolymer. In a particular embodiment of the present invention, the hot melt adhesive composition includes an additive which comprises a combination of a) a low molecular weight styrene-maleic anhydride ester resin and b) a low molecular weight maleated polybutadiene resin. The combination additive comprising a low molecular weight styrene-maleic anhydride ester resin and a low molecular weight maleated polybutadiene resin can be added to any conventional hot melt adhesive formulation, such as an adhesive resin of the group consisting of styrene-isoprene-styrene (SIS) block copolymers, hydrocarbon tackifying resins, polyacrylate resins, poly ethylene vinyl acetate (EVA) resins, polystyrene butadiene resins, random styrenebutadiene (SBR) copolymers, styrene-butadiene-styrene (SBS) block copolymers, styrene-ethylene-butylene-styrene (SEBS) block copolymers, amorphous poly-α olefin (APAO) resins, and a process oil, or mixtures thereof. By definition, the components of the said additive composition as defined above are excluded from these adhesive components (adhesive resin).

The additive or additive combination, as defined above, is added during the compounding of the adhesive. When an additive combination is used, such as a combination of a low molecular weight styrene-maleic anhydride copolymer ester and a low molecular weight maleated polybutadiene, the components of the additive can be added in varying amounts. In some embodiments, from 0 to about 15 weight percent of each component of the additive is used under the condition that when 0 is used for one polymer component at least one other polymer component is necessarily present. For an embodiment employing a low molecular weight styrene-maleic anhydride copolymer ester and a low molecular weight maleated polybutadiene as components of the said adhesive additive, preferably from about 1 to about 12 weight percent of each component is used. More preferably, the global weight content of the said additive composition (total weight

content of all polymers of said additive composition) in the said hot melt adhesive composition is generally of at least 3%.

An exemplary conventional hot melt adhesive, to which the additive of the present invention may be added, includes a styrene-isoprene-styrene (SIS) block copolymer, a hydrocarbon (C5 or C9) resin, rosin ester tackifiers, and/or a process oil. A SIS block copolymer may be employed in the hot melt adhesive, such as that which is sold by Kraton Performance Polymers Inc. of Houston, TX under the trade name Kraton D-1163. A C5 hydrocarbon tackifying resin may be utilized, such as that which is sold by Cray Valley U.S.A. of Exton, PA under the trade name Wingtack ET. A napthenic process oil, i.e. mineral oil, may be used in the hot melt adhesive as well, such as the one sold under the trade name Calsol 5550 by Calumet Specialty Products Partners, L.P. of Indianapolis, IN. As is known to one skilled in the art, conventional hot melt adhesive may include a variety of other components including, but not limited to, starches, waxes, plasticizers, anti-oxidants, stabilizers, pigments, dyes, biocides, flame retardants, antistatic agents, or fillers. For example, the hot melt adhesive may include Irganox 1010, an antioxidant sold by Ciba/BASF.

The additive of the present invention may be introduced to a conventional hot melt adhesive by any process known to one skilled in the art. For example, when SMA ester and maleated polybutadiene are employed as the additive polymers, they may be introduced separately from each other and separate from, or in combination with, any of the individual components of the conventional hot melt adhesive. As a further example, the additive may be introduced to the components of a conventional hot melt adhesive comprising a styrene-isoprene-styrene (SIS) block copolymer, a hydrocarbon (C5 or C9) resin, and rosin ester tackifiers after the components are heated above their individual melting points. The SMA ester may be a commercially available low molecular weight product with high maleic anhydride contents, such as that sold by Cray Valley U.S.A. of Exton, PA under the trade name SMA. The maleated polybutadiene may similarly be a commercially available product, such as that sold by Cray Valley U.S.A. of Exton, PA under the trade name Ricon. A process oil, such as mineral oil, may be added last. The hot melt adhesive containing the additive is allowed to mix on the

roll mill until it is homogeneous.

In another embodiment, the present invention is a hot melt adhesive label. The hot melt adhesive composition can be used in hot melt adhesive labels, preferably in hot melt pressure sensitive adhesive labels, particularly for recyclable glass articles which may be containers such as bottles. The labels can be removed with caustic, for example in a hot caustic bath, when the objects are recycled. Without being held to the theory, it is believed that the acid and/or anhydride groups of the additive impart caustic solubility to the otherwise insoluble other adhesive components such as styrene-isoprene-styrene (SIS) tri-block copolymer, hydrocarbon tackifying resin, and/or process oil. The present invention enables the manufacturing of a hot melt adhesive which has favorable water resistance and viscoelastic properties for adhesion to a substrate, for example the retention of a label on a glass bottle, while also imparting caustic removability to the hot melt adhesive formula. This allows for strong retention and adhesion characteristics when they are desired, but also removability of the hot melt adhesive from the substrate when it is necessary as in the recycling process.

The hot melt adhesive containing the additive may be applied to the label and/or the substrate by various processes known to one skilled in the art. In one representative process, the caustic removable hot melt adhesive of the present invention is melted and poured onto a blade coater. The blade coater can be employed to apply a thin film of the caustic removable hot melt adhesive to a release liner to which a face stock is laminated. The laminate may then be cut into label size strips for application to a substrate, such as a glass bottle.

In a further embodiment, the present invention is an article having a label adhered with a caustic removable hot melt adhesive composition containing an additive as defined above according to the invention. For hot melt adhesive labels, particularly for hot melt pressure sensitive adhesive labels, the adhesive is coated onto a release liner, which is then immediately laminated with a label face stock, which could be paper or plastic. The label is then applied to an article such as a glass bottle for identification and/or decorative purposes. After the contents of the article have been used, it may be desirable to recycle the article. To remove the label, articles can be placed in a hot caustic bath, which causes the adhesive to

dissolve and/or delaminate from the article. The clean bottle or other article can then more easily be recycled without the contamination of the label and/or the adhesive. Until now, it has not been possible to remove conventional hot melt adhesive labels from articles in this way. Removal of the hot melt adhesive is made possible by adding the combination additive of the present invention.

The advantageous properties of this invention can be observed by reference to the following examples, which illustrate but do not limit the invention.

EXAMPLES

The following resins are used in combination as the additive according to the invention : (a) a low molecular weight product with high maleic anhydride contents sold by Cray Valley under the tradename "SMA", which has a styrene : maleic anhydride (S : MA) ratio of 1.5:1, a number average molecular weight (Mn) of 2,900 and a weight average molecular weight (Mw) of 7,000, which is esterified with a (45% / 30%) cyclohexyl / isopropyl ester of a styrene-maleic anhydride (SMA) copolymer to an esterification ratio of 75%; and (b) a low molecular weight maleated polybutadiene sold by Cray Valley under the tradename "Ricon", which has a number average molecular weight (Mn) of 7,500, a weight average molecular weight (Mw) of 10,000, and is 20% w/w maleated. The molecular weight ranges are as measured by gel permeation chromatography (GPC) with polystyrene standards in tetrahydrofuran (THF).

The caustic removable hot melt adhesive with additive was prepared in the following general manner. During the process of making a conventional hot melt adhesive, styrene-isoprene-styrene (SIS) block copolymer, hydrocarbon (C5 or C9) resin, and rosin ester tackifiers are heated to above their individual melting points. The melted resins are then combined on a heated roll mill. Between 0 - 11 wt % of the SMA ester was added after the Kraton D-1163 SIS block copolymer, and 0 - 11 wt % of the maleated polybutadiene is added along with the Wingtack ET hydrocarbon tackifying resin. Calsol 5550 mineral oil is added last. The mixtures were allowed to mix on the roll mill until they were homogeneous, at which point they were removed from the mill into a carton. Table 1, below, shows the hot melt adhesive formulations which were tested. Sample 1 is used as the

control for the tests, as that hot melt adhesive formulation contains neither the SMA ester or the maleated polybutadiene.

TABLE 1. Sample Formulas Tested (in w/w%)

Sample Formula	SIS Block Copolymer (Kraton D-1163)	Hydrocarbon tackifying resin (Wingtack ET)	Mineral Oil (Calsol 5550)	Antioxidant (Irganox 1010)	Additive		
					Total Weight % of Additive	Styrene-maleic Anhy-dride (SMA)	Maleated Polybuta-diene (RICON)
1 (Control)	34.65	54.46	9.90	0.99	0.00	0.00	0.00
2	33.33	52.38	9.52	0.95	3.80	1.90	1.90
3	32.11	50.46	9.17	0.92	7.34	3.67	3.67
4	29.91	47.01	8.55	0.85	13.68	6.84	6.84
5	30.97	48.67	8.85	0.88	10.62	10.62	0.00
6	30.97	48.67	8.85	0.88	10.62	0.00	10.62

The sample formulas were initially tested for compatibility. It is noted that the combination additive of the present invention was found to be compatible with the components of conventional hot melt adhesives. The caustic removable hot melt adhesive with additive mixed uniformly during compounding with a Sigma mixer. There was no phase separation at room temperature or in the 170°C oven-heated samples (i.e., uniform cross-section).

Dynamic Mechanical Analysis was also performed on the samples, using a TA Instruments Rheometer AR 2000 on an 8 mm parallel plate. Dynamic Mechanical Analysis (DMA) is a thermoanalytical technique, which is well known to one having ordinary skill in the art, and is used to study the characteristics of materials, such as the viscoelastic nature of polymers. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. The samples can be either solids, which are tested by linearly applied strains, or melts or liquids, which are normally tested in shear. The DMA sample deforms under the applied load. From this the stiffness of the sample can be determined, and the sample modulus can be calculated. It is possible to determine the damping properties of a material by measuring the time lag in the

displacement compared to the applied force. The time lag is reported as a phase lag angle. The damping is called tan delta (δ), as it is reported as the tangent of the phase lag.

Viscoelastic materials such as polymers typically exhibit the properties of a glass (high modulus) at low temperatures, and those of a rubber (low modulus) at higher temperatures. This change of state, i.e., glass transition or alpha relaxation, can be observed by scanning the temperature during a DMA experiment. The samples were observed for broadening of the tan δ peak, and/or the appearance of a second peak indicating a change of state, under the DMA. Table 2, below, presents the results of the Dynamic Mechanical Analysis.

TABLE 2. Dynamic Mechanical Analysis

Sample Formula	Temp (°C)	Tan (δ)	Temp 1st X-over (°C)	Storage Modulus G' (Pa)	Temp 2nd X-over (°C)	Storage Modulus G' (Pa)	Temp 3rd X-over (°C)	Storage Modulus G' (Pa)
1 (Control)	8	2.801	-7.6	$1.53*10^7$	23.1	60580	102.7	8824
2	8.1	2.755	-7.9	$1.78*10^7$	22.8	64160	102.1	8299
3	7.2	2.744	-8.5	$1.53*10^7$	22.6	64420	101.8	8454
4	8	2.729	-7.6	$1.58*10^7$	23.5	62480	101.5	8029
5	8.1	2.907	-7.9	$1.81*10^7$	23.6	65790	99.3	7811
6	8.1	2.733	-8	$1.54*10^7$	23.9	53240	101.9	7089

The cross-over temperatures identified by the Dynamic Mechanical Analysis correspond to the temperatures at which the G' storage modulus equaled the G'' loss modulus. This is measured as a function of temperature from -50 to 125°C by the DMA, at a temperature scan rate of 4°C per minute and at a frequency of 1 Hz.

Table 2 shows that the samples formulas containing the additive yielded good initial compatibility results with the conventional hot melt composition of sample formula 1 (i.e., the control). As can be seen from Table 2, the sample formulas containing the additive exhibited similar DMA peaks (i.e. tan delta and cross-over temperature points) as the conventional hot melt composition of sample formula 1. Sample formulas 5 and 6, containing only one part of the combination additive, showed suitable but less favorable initial compatibility results. As such,

when an SMA ester is selected as the low molecular weight maleic anhydride, a maleated polybutadiene is used in combination with the SMA ester to make the additive compatible with conventional hot melt adhesives. The overall results as shown in Table 2, also demonstrate that the essential viscoelastic performances of the adhesive composition are not significantly affected when the additive as defined according to the present invention is added to a conventional hot melt adhesive.

In addition to the Dynamic Mechanical Analysis test for initial compatibility, the compatibility of the additive with the conventional hot melt adhesive was tested and confirmed by additional independent methods. Visual observations were made of the formulations in a Sigma mixer. Under this method, the formulations were deemed compatible if there was an absence of visible phase separation. The adhesives were uniformly mixed during their compounding with the additive of the invention, and no visible phase separation was identified. Next, visual observations were made of oven heated samples, heated to 170°C. Again, an absence of visible phase separation was an indicator of compatibility. No phase separation was seen in the oven heated samples for the additive of the invention. Finally, visual observations were made of the applied film during coating. Under this method, a clear adhesive film was deemed compatible while a cloudy adhesive film was deemed incompatible. The results showed compatible clear adhesive films for the adhesive of the invention containing the additive.

The adhesive label of the present invention may be prepared by various methods known to one having ordinary skill in the art. In a separate step, the adhesive is melted and poured onto a blade coater so that a thin film of it can be applied to a release liner to which a face stock is laminated. The laminate is then cut into label size strips. To test the label, the release liner is removed and the label is applied to a substrate and rolled with a 4 lbs roller. Typical adhesive properties such as tack, peel and shear can be measured and compared with adhesives not containing the combination additive of the present invention. For adhesion tests, the adhesives were heated to 170°C and coated onto a release liner and immediately laminated to a 1 mm thick polyethylene terephthalate film. The initial adhesive properties were measured after aging the coated adhesive

sheets for 24 hours at 25°C and 75% humidity. Aged adhesive properties were measured after aging the coated sheets for 1 weeks at 70°C. The aged adhesion results, when compared to the initial adhesion properties, showed that the adhesion properties were equivalent or improved.

The sample formulas were tested using standard test methods established by the Pressure Sensitive Tape Council (PSTC). The sample formulas were also tested for peel strength, according to PSTC Method 101 "International Standard for Peel Adhesion of Pressure Sensitive Tapes". Peel adhesion is the force required to remove a pressure sensitive tape from a test panel or its own backing at a controlled angle and at a standard rate and condition. The sample formulas were tested on high density polyethylene (HDPE), stainless steel (SS), and glass substrates for 180 degree peel adhesion. The sample formulas were further tested on HDPE, SS, and glass substrates for loop tack under PSTC Method 16. The results of these tests are shown in Table 3 below.

TABLE 3. Initial Adhesion Performances

Sample Formula	SMA / RICON	Total Additive %	Peel Adhesion on SS kN/m (lbf/in)	Peel Adhesion on Glass kN/m (lbf/in)	Peel Adhesion on HDPE kN/m (lbf/in)	Loop Tack Adhesion on SS kN/m (lbf/in)	Loop Tack Adhesion on Glass kN/m (lbf/in)	Loop Tack Adhesion on HDPE kN/m (lbf/in)
1 (Control)	0 / 0	0	1.38 (7.91)	1.37 (7.84)	0.658 (3.76)	1.45 (8.27)	1.48 (8.43)	0.429 (2.45)
2	1.90 / 1.90	3.80	0.905 (5.17)	0.770 (4.4)	0.564 (3.22)	1.22 (6.94)	1.21 (6.9)	0.443 (2.53)
3	3.67 / 3.67	7.34	0.932 (5.32)	0.960 (5.48)	0.597 (3.41)	1.29 (7.37)	1.19 (6.82)	0.529 (3.02)
4	6.84 / 6.84	13.68	0.937 (5.35)	0.799 (4.56)	0.437 (2.5)	1.13 (6.46)	1.11 (6.31)	0.416 (2.38)
5	10.62 / 0	10.62	0.870 (4.97)	0.662 (3.78)	0.340 (1.97)	0.905 (5.17)	0.893 (5.1)	0.327 (1.87)
6	0 / 10.62	10.62	0.668 (3.82)	0.672 (3.84)	0.510 (2.91)	0.996 (5.69)	1.07 (6.1)	0.452 (2.58)

As known by one having ordinary skilled in the art, the adhesive ingredients may be adjusted to achieve specifically desired adhesion properties. The amount of the low molecular weight α,β-unsaturated acid anhydride polymer can be varied to balance adhesion characteristics and initial compatibility with conventional hot melt formulations, while increasing water-resistance and caustic removability. For

example, when a combination of SMA ester and maleated polybutadiene is used as the additive, a limited and acceptable decrease in overall adhesive properties was identified by the peel and loop tack tests. However, the combination additive was very compatible with conventional hot melt adhesive formulas containing SIS block copolymers, hydrocarbon resins, tackifier resins, and mineral oil with overall unaffected viscoelastic performance metrics, as shown in Table 1 above. This can effectively be seen by the results from the Dynamic Mechanical Analyses in Table 1, which show no significant change between the formulas containing the additive and the control formula (sample formula 1) containing no additive.

The combination additive of the present invention was found to be compatible with the conventional hot melt adhesives while also enabling them to be caustic removable. This additional characteristic is useful for many purposes, particularly in the recycling process. To determine this inventive feature, the samples were tested for caustic removability. The adhesives were heated to 170°C and coated onto 30.48 cm by 2.54 cm (12 inch by 1 inch) adhesive strips of unbleached Kraft 30 lbs/ream paper to test caustic removability and cold water resistance. The labels were adhered to flat glass panels and rolled with a 4 lbs roller. The glass panels were immersed in a hot caustic bath consisting of 2.5% sodium hydroxide in water, heated to 80°C. Slight agitation was applied to the caustic bath.

The samples were timed for how long it took for the labels to remove from the panels and the adhesion was rated for the amount of adhesive residue left on the panels. Glass panels are kept immersed in the aqueous solution of NaOH at 2.5% at 80°C for 5 minutes. Then, the strip adhesion (i.e., caustic removability) is measured and given a rating from 0 to 5, where 5 represents easy removal from the panel and no adhesive left on the panel and 0 represents no removal of the test strip (i.e., the adhesive remains on the substrate). The results below show that only the sample of composition 4 (with 6.84 w% of each component of the additive and 13.68 w% of global additive) is easily removable with a rate of 5 on glass.

TABLE 4. Caustic Removability Tests

Sample Formula	SMA / Ricon Maleated Polybutadiene	Total Additive (w%)	Rate of Removability
1 (Control)	0/0	0	0
2	1.90/1.90	3.80	3
3	3.67/3.67	7.34	2
4	6.84/6.84	13.68	5
5	10.62/0	10.62	2
6	0/10.62	10.62	3

While preferred embodiments of the invention have been shown and described herein, it will be understood that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions will occur to those skilled in the art without departing from the spirit of the invention. Accordingly, it is intended that the appended claims cover all such variations as fall within the spirit and scope of the invention.

The present invention, therefore, is well adapted to carry out the objects and attain the ends and advantages mentioned, as well as others inherent therein. While the invention has been depicted and described and is defined by reference to particular preferred embodiments of the invention, such references do not imply a limitation on the invention, and no such limitation is to be inferred. The invention is capable of considerable modification, alteration and equivalents in form and function, as will occur to those ordinarily skilled in the pertinent arts. The depicted and described preferred embodiments of the invention are exemplary only and are not exhaustive of the scope of the invention. Consequently, the invention is intended to be limited only by the spirit and scope of the appended claims, giving full cognizance to equivalents in all respects.

CLAIMS

1. An additive composition for imparting caustic removability to a hot melt adhesive, wherein the said additive composition comprises, at least one, preferably at least two, low molecular weight polymer (or resin) containing in its composition at least one α, β ethylenically unsaturated carboxylic anhydride or acid, preferably the said polymer being selected from low molecular weight copolymers or homopolymers, preferably copolymers more preferably partial esters of copolymers, of the said anhydride or acid and from low molecular weight polymers grafted with the said anhydride or acid.

2. An additive composition according to claim 1, wherein the said polymer, containing said anhydride or acid, has a molecular weight (Mw) of less than 50,000.

3. An additive composition according to claims 1 or 2, wherein the said anhydride or acid is selected from maleic anhydride, fumaric acid, itaconic anhydride or acid or tetrahydrophthalic anhydride or acid, preferably from maleic anhydride and fumaric acid, and more preferably maleic anhydride.

4. An additive composition according to any one of claims 1 to 3, wherein the said copolymer is a copolymer of the said anhydride or acid, with at least one comonomer selected from : vinyl aromatic monomers, ethylene and/or propylene, preferably at a molar ratio of said comonomer to said anhydride or acid ranging from 1/1 to 2/1.

5. An additive composition according to claim 4, wherein the said copolymer is a styrene-maleic anhydride copolymer.

6. An additive composition according to any one of claims 1 to 5, wherein the said grafted polymer is selected from diene homopolymers and/or copolymers or from ethylene homopolymers and/or copolymers or from propylene homopolymers and/or copolymers or from tackifying resins, preferably with a weight content of said anhydride or acid ranging from 10 to 50%, preferably from 10 to 30%.

7. An additive composition according to claim 6, wherein the said grafted polymer is a maleated polymer (polymer grafted with maleic anhydride).

8. An additive composition according to claims 6 or 7, wherein the said grafted

polymer is a maleated diene homopolymer (polydiene) or copolymer the said diene, the said diene being selected from butadiene and/or isoprene, and preferably is a maleated polybutadiene or a maleated polyisoprene and more preferably is a maleated polybutadiene.

9. An additive composition according to any one of claims 1 to 8, wherein it comprises at least two of said polymers containing the said α, β ethylenically unsaturated carboxylic anhydride or acid, as defined according to any one of the claims 1 to 8.

10. An additive composition according to claim 9, wherein it comprises at least the following two polymers (or resins) a) and b) :

a) at least one low molecular weight partial ester of a copolymer of said anhydride or acid, as defined according to any one of claims 2 to 5

b) at least one low molecular weight polymer grafted by said anhydride or acid, as defined according to any one of claims 6 to 8.

11. An additive composition according to claim 10, wherein the said copolymer a) is a low molecular weight partial ester of a maleic anhydride-vinyl aromatic monomer copolymer, preferably styrene-maleic anhydride copolymer and wherein the said grafted polymer b) is a low molecular weight maleated diene homopolymer or copolymer, preferably maleated polybutadiene or maleated polyisoprene.

12. An additive composition according to claims 10 or 11, wherein the said polymer or resin a) is a low molecular weight partial ester of a styrene-maleic anhydride (SMA) copolymer resin and the said polymer or resin b) is a low molecular weight maleated polybutadiene resin.

13. An additive composition according to any one of claims 10 to 12, wherein the said polymer a) is a partial ester of a styrene-maleic anhydride copolymer with a styrene to maleic anhydride S/MA molar ratio ranging from 1/1 to 2/1, preferably 1.4/1 to 1.6/1, preferably being monoesterified by at least one monoalcohol selected from C1 to C12, more preferably C2 to C8 monoalcohols, optionally alkoxylated.

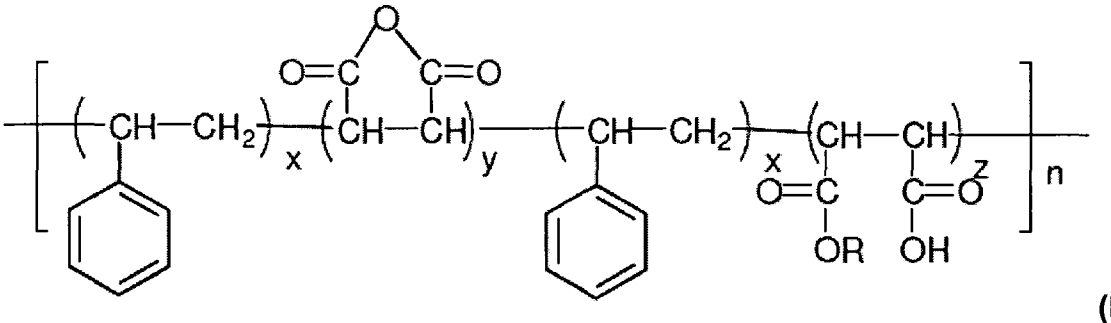
14. An additive composition according to claim 13, wherein the said polymer a) has a monoesterification ratio of the said anhydride from 50 to 100%.

15. An additive composition according to any one of claims 10 to 14, wherein the said polymer a) has a molecular weight ranging from 1,000 to 50,000 and the said polymer b) has a molecular weight ranging from 1,000 to 25,000, preferably from 2,000 to 10,000.

16. An additive composition according to any of claims 10 to 15, wherein the said polymer b) comprises from 10 to 50% preferably from 10 to 30% by weight of maleic anhydride.

17. An additive composition according to any one of claims 1 to 16, wherein the said polymers containing said anhydride or acid are soluble at any degree in basic pH solutions at pH higher than 8.

18. An additive composition according to any one of claims 10 to 17, wherein the said polymer or resin a) is according to the following formula (I) :

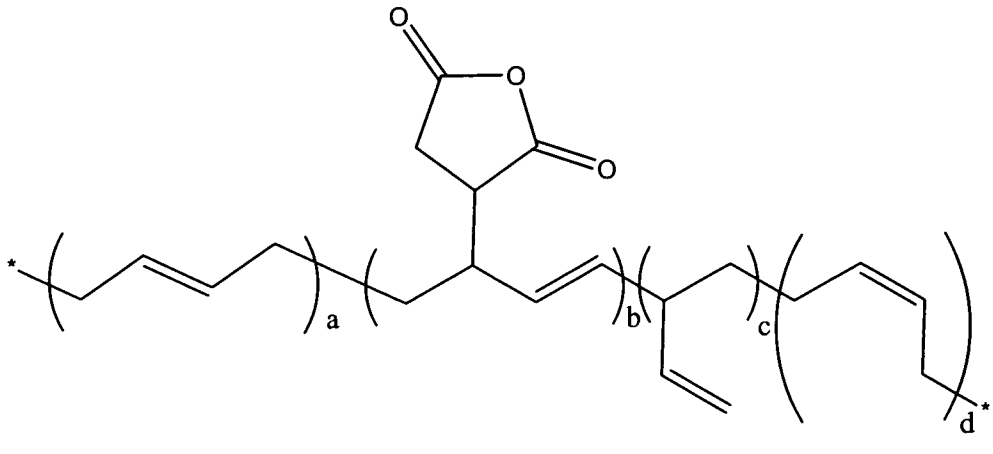


(I)

in which, R is a residue of at least one monoalcohol selected from C1 to C12 monoalcohols, optionally alkoxylated, and their mixtures, with a molar ratio S/MA (or x/ (y+z)) varying from 1/1 to 2/1, preferably 1.4/1 to 1.6/1, n ranging from 7 to 72, and a ratio of monoesterification z/(y+z) ranging from 50 to 100%.

19. An additive composition according to any one of claims 10 to 18, wherein the weight ratio between the said polymer a) and the said polymer b) ranges from 40/60 to 60/40.

20. An additive composition according to any one of claim 12 to 19, wherein the said maleated polybutadiene is according to formula (II) :



(II)

with "a" representing trans 1,4 polybutadiene units, "b" maleated polybutadiene units, "c" polybutadiene units with pending vinyl group (1,2 addition) and "d" representing cis 1,4 polybutadiene units.

21. A hot melt adhesive composition, preferably a pressure sensitive hot melt adhesive composition, wherein it comprises an additive composition as defined according to any one of claims 1 to 20, as an adhesive additive component.

22. A hot melt adhesive composition according to claim 21, wherein it comprises the said additive composition at a global weight content of at least 3%.

23. A hot melt adhesive composition according to claims 21 or 22, wherein it further comprises an adhesive resin of the group consisting of styrene-isoprene-styrene (SIS) block copolymers, hydrocarbon or rosin ester tackifying resins, polyacrylate resins, poly ethylene vinyl acetate (EVA) resins, polystyrene butadiene resins, random styrene-butadiene (SBR) copolymers, styrene-butadiene-styrene (SBS) block copolymers, styrene-ethylene-butylene-styrene (SEBS) block copolymers, amorphous poly-α olefin (APAO) resins, and optionally a process oil, or mixtures thereof.

24. A hot melt adhesive composition according to any one of claims 21 to 23, wherein the said additive composition is a defined according to any one of claims 9 to 20.

25. A hot melt adhesive label, preferably a pressure sensitive hot melt adhesive label, wherein it is applied on the said label or on the substrate or on the article on which the said label is adhered to, a hot melt adhesive composition as defined according to any one of claims 21 to 24.

26. A label according to claim 25, wherein it is a pressure sensitive hot melt

adhesive label.

27. Use of an additive composition as defined according to any one of claims 1 to 20, preferably as defined according to any one of claims 9 to 20, as an adhesive additive component in holt melt adhesive compositions for imparting caustic removability to resulting adhesives or adhesive labels.

28. Use of an adhesive composition as defined according to any one of claims 21 to 24, for caustic removable adhesives or caustic removable adhesive labels.

29. Use according to claims 27 or 28, wherein it is for recycling articles on which the said adhesives or said adhesive labels are applied.

30. An article comprising a label adhered thereto, wherein said label is as defined according to claims 25 or 26.

31. An article according to claim 30, wherein it is a recyclable article.

32. An article as defined according to claim 31, wherein it is a container for a consumable product and wherein the said label is removable with caustic solution without leaving adhesive on the said article.

33. An article as defined according to any one of claims 30 to 32, wherein it is a glass article, preferably a glass bottle.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/002043

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J11/08 C08L35/06 C08L51/04 C08L51/06
ADD.

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)
C08L C09J

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)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/108739 A1 (VALETTE LUDOVIC [FR]) 8 May 2008 (2008-05-08) claims 1,2,3 page 2, left-hand column, paragraph 16 page 2, left-hand column, paragraph 19 - paragraph 20 page 6, right-hand column, paragraph 76 - paragraph 78	1-18,20
X	US 3 365 411 A (MERTZWEILLER JOSEPH K ET AL) 23 January 1968 (1968-01-23) column 2, line 35 - line 45 column 4, line 1 - line 10 column 4, line 50 - column 5, line 6 column 5, line 70 - column 6, line 4 column 6, line 5 - line 33	1-4, 6-10,15, 16,19,20

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[X] Further documents are listed in the continuation of Box C. [X] See patent family 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	Date of mailing of the international search report
16 July 2010	27/07/2010

Name and mailing address of the ISA/	Authorized officer
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International application No
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