

Description

The present invention relates to adhesive compositions which comprise an acrylate- or methacrylate-based ester component.

- 5 As the terms are used herein, acrylate- and methacrylate-based adhesives are based on the respective chemical structures



- 10 The adhesives may be based on acrylic acid or methacrylic acid ($\text{R}=\text{H}$) or on methyl acrylate or methyl methacrylate ($\text{R}=\text{CH}_3$).

- US-A-3890407, US-A-4112013, US-A-4118436, US-A-4126504, US-A-4127699, US-A-4182644, US-A-4223115, US-A-4226954, US-A-4263419 and US-A-4293665 disclose acrylate- or methacrylate-based adhesives including chlorosulfonated polyethylene. In some cases, it is indicated that the presence of the chlorosulfonated polyethylene provides desirable properties such as the substantial avoidance of any need to mix composition ingredients prior to use, the relatively fast setting of the composition, the formation of strong, durable bonds, and adhesion of oily metal surfaces.

- Polymers comprising relatively long sequences or chains of at least two different monomers or monomeric units can have such chains linked together in a "block" or "graft" arrangement. A block arrangement is linear and is formed from at least two alternating monomeric units. The block arrangement, moreover, can further be formed from monomeric unit sequences which alternate (or repeat) in either an ordered or a random fashion. See US-A-4,332,858. Block or graft polymers are often referred to as co-polymers, terpolymers or multi-component polymers.

- In the graft arrangement, one or more of such sequences are grafted onto a backbone of yet another sequence, such grafting usually taking place at each one of a plurality of grafting sites of the backbone. See, for example, *Textbook of Polymer Science*, 2nd Edition, by F. W. Billmeyer, Jr., published by Wiley-Interscience, a Division of John Wiley and Sons, Inc. (1971), at pp. 350-351. In the graft co-polymer art, when the backbone is a rubber or a rubber-like material and the grafted sequences are vinyl or acrylate- or methacrylate-based monomers, the backbones are often referred to as the "core" of the graft co-polymer. Sequences grafted onto the core form a "Shell" there surrounding.

- Such graft co-polymers, frequently referred to as resins, often take the form of a plurality of relatively small particles, especially when the rubber or rubber-like material or the grafted portions or both of these are crosslinked. Not all graft co-polymer resins have such a core-and-shell configuration (or morphology), however. Some, for example, may have a more continuous (i.e., homogeneous) microstructure which, quite often, takes the form of interpenetrating (yet distinct) polymer networks.

- Graft co-polymer resins which have the core-and-shell configuration are currently primarily used as modifiers in certain polymer systems. For example, certain ABS (acrylonitrile-butadiene-styrene) or MBS (methacrylate-butadiene-styrene) resins, when added to PVC (polyvinyl chloride), are well-known impact-resistance or processability modifiers.

- Graft co-polymers, per se, are generally not added to adhesive compositions to augment or enhance the adhesive qualities thereof. For example, although US-A-3,870,675 discloses (at column 2, lines 6-27) that an acrylate-based or methacrylate-based adhesive composition can include an ABS resin, the ABS resin therein is included primarily because of its rubber-like characteristics. Certain types of ABS resin, moreover, are well known rubber-like materials and, accordingly, are often used interchangeably with other rubber-like materials. Such types of ABS resin, furthermore, are known to be two-phase systems comprising inclusions of a rubber or a rubber-like phase in a continuous, glassy phase, wherein the continuous phase forms a matrix for the two-phase system. It is further well known that obtaining preferred rubber-like qualities, as to such types of ABS resin, requires selectively grafting, as between the continuous and rubber or rubber-like phases thereof. See, for example, *Textbook of Polymer Science*, cited above, at page 408.

- Further, US-A-3870675 (see column 2, lines 15-19 in connection with column 3 lines 42-45 and column 6, Table 3) discloses compositions in which other rubber-like materials have been substituted for ABS. The adhesive compositions of US-A-3870675 have properties, such as tensile strength after contact, shear strength and impact strength, which make their application and use quite different from the chlorosulfonated polyethylene-based compositions described above.

- US-A-4287106 discloses an acrylate-based or methyl acrylate-based adhesive composition including ABS polymers (see column 2 lines 33-48), but specifically teaches away from the inclusion of chlorosulfonated polyethylene (column 1 lines 14-34 in connection with column 1 lines 57-68, column 2 lines 1-32, column 8 lines 41-56 and column 9 lines 50-64). More specifically, US-A-4287106 discloses that a chlorosulfonated amide or imide produces an adhesive composition having certain desirable properties.

- Hitherto, it has been thought that the addition of, say, a chlorosulfonated polyethylene to an acrylate- or methacrylate-based adhesive composition having desirable properties would adversely affect those properties.

- EP-A-0025015 discloses an adhesive composition comprising an acrylate- or methacrylate-based

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ester monomer, a catalyst, an organic sulfonyl chloride and a graft copolymer resin. Such compositions are particularly directed to the bonding of zinc-covered steel automobile parts.

An adhesive composition according to the present invention comprises an acrylate-based or (preferably) a methacrylate-based ester monomer; a catalyst; a chlorinated polyethylene plus an organic sulfonylchloride, or a chlorosulfonate polyethylene; and a graft copolymer resin in the form of particles having a rubber-like core and a relatively hard shell.

The ester monomer is preferably methyl, ethyl, butyl, cyclohexyl, 2-ethylhexyl or tetrahydrofuryl methacrylate, among which the methyl and ethyl esters are more preferred and methyl methacrylate is most preferred.

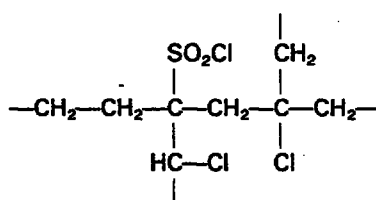
In certain instances, it is desirable that the methacrylate-based ester monomer should include an effective amount of an inhibitor for inhibiting or otherwise preventing polymerization of the ester monomer. For example, below-presented examples of the composition of the present invention, which therein included methyl methacrylate ester monomer, generally contained from about 50 to about 90 parts per million (ppm) of hydroquinone in the ester monomer as such an inhibitor. Throughout this application the term ppm is based on total weight of the named material. In this sense, the term translates into inclusion of from about 50 to about 90 parts by weight of hydroquinone per million parts by weight of ester monomer, the monomer weight being based upon methyl methacrylate and including the hydroquinone.

The composition can further include an acrylate-based acid monomer such as acrylic acid. Inclusion of an acid monomer, however, is entirely optional. In certain instances it may be desirable to exclude use of the acid monomer. See, for example, below-presented discussion which is directed to explanation of Example VI. Preferably, however, the composition further includes methacrylic acid. Such methacrylic acid, moreover, in below-presented examples (of the compositions of the present invention), generally contained, for reasons discussed immediately above, about 250 ppm of hydroquinone in the acid monomer as an inhibitor.

The composition further includes a catalyst. For purposes of the present invention, the term "catalyst" means a free-radical generator. As discussed in above-cited US-A-4,112,013 at column 2, lines 23-24 thereof, such a free-radical generator can be an organic peroxide, an organic hydroperoxide, a perester, or a peracid. As is well known in the field of acrylate-based and methacrylate-based compositions, such a catalyst is used for triggering polymerization of acrylate-based and methacrylate-based monomers. A preferred catalyst, appearing in below-presented examples of the compositions of the present invention, is cumene hydroperoxide, a free-radical generating organic hydroperoxide.

The composition additionally includes either chlorinated or chlorosulfonated polyethylene polymer resin. I have found, on previous occasion (see, for example, US-A-3,890,407), that chlorinated polyethylene can be substituted for chlorosulfonated polyethylene. When chlorinated polyethylene is substituted, however, an organic sulfonyl chloride is further included.

Preferably, however, the composition of the instant invention includes chlorosulfonated polyethylene polymer, the resin which, in turn, preferably contains from about 25 to about 70 weight percent chlorine and from about 3 to about 160 millimoles of sulfonyl chloride moiety per 100 grams thereof. Such polymer resin is described more fully in the US patents 3,890,407, 4,112,013 and 4,182,644. Briefly paraphrasing, the polyethylene from which the chlorosulfonated polyethylene is prepared should have a melt index of from about 4 to about 500. A preferred chlorosulfonated polyethylene polymer resin is prepared from branched polyethylene and has a chemical structure resembling



An especially preferred chlorosulfonated polyethylene (CSPE) polymer resin is marketed under the Trade Mark "Hypalon 30". It contains about 43% by weight chlorine, about 1.1% by weight sulfur and about 34 millimoles of sulfonyl chloride moiety per 100 grams of polymer resin. It is known to be made from branched polyethylene having a melt index of about 100.

Table I gives the properties of preferred varieties of CSPE sold under the "Hypalon" Trade Mark, which are currently commercially-available from E. I. Du Pont de Nemours & Co., Wilmington, Delaware 19898, USA.

TABLE I (percentages by weight)

	"Hypalon" CSPE Type	30	20	LD-999	48S
5	Chlorine content (%)	43	29	35	43
	Sulfur content (%)	1.1	1.4	1.0	1.0
	Specific gravity	1.27	1.12	1.18	1.26
10	Mooney viscosity at 100°C	30	28	30	62
	Brookfield viscosity (mPa-S)				
	25% in toluene	400	1300	—	—
15	5% in xylene	4	9	18	12

The composition also preferably includes a catalyst activator (or initiator). Throughout this application, the terms "activator" or "initiator" are used interchangeably and generally mean an aldehyde-amine condensation product, organic sulfonyl chlorides or mixtures thereof. For example, such a condensation product can be made from butyraldehyde and a primary amine, such an amine being, for example, aniline or butylamine.

On the other hand, certain well known catalysts (e.g. heat-activatable peroxides or azodiisobutyronitrile), when heated above room temperatures to induce their decomposition, are known to catalyze (without the preferred catalyst activators being present), thereby causing polymerization of the monomers; and inclusion (in the composition) of catalyst activators (or initiators) is therefore not crucial. However, certain well known promoters (e.g. cobalt, copper and other transition metal compounds) are often added to aid heat induced peroxide decomposition.

Furthermore, ultraviolet light and other forms of radiant energy may be used instead of heat to induce polymerization in the absence of the preferred activators. See, for example, *The Chemistry of Organic Film Formers*, by D. H. Solomon, published by Robert E. Krieger Publishing Co. (1977), at pages 12—14; and *Plastics Polymer and Science Technology*, edited by M. D. Bajjal, published by John Wiley & Sons (1982) at pages 604—605.

In general, however, the present invention includes activators. Condensation products of aliphatic aldehydes with aliphatic or aromatic amines, moreover, are preferred as such activators.

In the absence of such condensation products, an organic substance having sulfonyl chloride moieties is preferred. Most preferably, however, the initiator (or activator) comprises a condensation product of butyraldehyde and aniline. One such butyraldehyde-aniline condensation product, marketed under the trademark "Vanax 808", is currently commercially available from the R. T. Vanderbilt Company, Inc., 230 Park Avenue, New York, NY, 10017.

Also usable as catalyst initiators, in combination with or in place of the above-described initiators, are the tertiary amines which I mention in above-cited US—A—4,112,013 (at column 2, lines 10—13).

The chlorosulfonated polyethylene polymer resin used contained sulfonyl chloride moiety which functions as a catalyst activator (or initiator). For certain adhesive compositions presented below, which do not include chlorosulfonated polyethylene polymer resin, certain organic sulfonyl chloride derivatives, such as, for example, propane sulfonyl chloride, or para-toluene sulfonyl chloride have been added to the adhesive composition to make up for the absence of sulfonyl chloride moiety.

The adhesive composition of the present invention further also includes a graft co-polymer resin. Generally speaking, the graft co-polymer resins of the present invention comprise particles of rubber or rubber-like cores or networks which are surrounded, and may even be encapsulated, by relatively hard shells.

Such graft co-polymer resins, moreover, as briefly discussed above, have generally been found useful as physical property-modifiers of PVC, or other normally-rigid plastics or the like. See, for example, US—A—3,845,164. Such physical property modifiers, moreover, have been found to increase flexibility and impact resistance of many normally-rigid plastics. In such a use, the graft co-polymer is generally a relatively small particle which, for example, can be dispersed throughout the normally-rigid plastic prior to injection molding thereof. Upon being thus dispersed throughout the plastic, the graft co-polymer resin particles, moreover, are generally not known to swell or otherwise react with the plastic.

In examples disclosed below, however, the preferred graft co-polymer particles have been observed to "swell" in size, and seem to react or otherwise interact with polymerizing monomeric components of the composition. Most ABS resins which are included in injection-moldable plastic compositions (for reasons outlined above), on the other hand, do not swell but rather appear to dissolve therein. As to the instant invention, however, when the preferred graft co-polymer resin particles were included in the below-presented adhesive compositions, it was observed that the preferred graft co-polymer particles generally swelled in size, became relatively gel-like and provided improved spreading and flow properties to the uncured adhesive compositions (discussed below).

Such improved flow properties are highly desirable in certain adhesive applications. For example, when an adhesive is applied to an article by means of a syringe-type applicator, many commercially available adhesives undesirably form a "string" of adhesive which generally extends from a first point on the article (where the adhesive was applied) to a second point (a subsequent position of the applicator) spaced from the first point. When the present invention was tested in just such an applicator, the flow properties of the present invention were such that a relatively small droplet of such adhesive was topically applicable to the point of application on the article to be bonded, with no adhesive string extending therefrom. Such a flow property of the present invention has also been tested for use in the field of adhesion of relatively small parts (for example, electronic parts) and the invention appears to be acceptable for such a use. During performance of the syringe-type applicator test, it was observed that certain effective, but relatively less-preferred graft co-polymer resins (e.g., ABS molding-grade resin) also appeared to dissolve in the methacrylate-based ester monomer.

In the instant invention, the methacrylate-based ester and methacrylate-based acid monomers polymerize and attach themselves to the chlorosulfonated polyethylene polymer resin particles. The mechanics of such attachment and polymerization are currently not completely known in detail. For example, it is not known to what extent attachment or polymerization occurs, nor is the order (of attachment and polymerization) known. At least some of these monomers, however, are believed to become attached during the initiation step of polymerization reaction or reactions.

The ester and acid monomers, moreover, are currently thought to penetrate the shell of individual graft co-polymer resin particles and polymerize therein thereby causing the shell or core or both to swell in size.

Regardless of theory, however, what has been observed when adhesive compositions comprising acrylate-based (preferably methacrylate-based) ester and acid monomers which have had chlorosulfonated polyethylene polymer and graft co-polymer resin particles included therewithin, is an adhesive composition having a surprising combination of enhanced overall adhesive and flow physical properties.

Preferred graft co-polymer resins are selected from the group consisting of acrylonitrile-butadiene-styrene (ABS), methacrylate-butadiene-styrene (MBS), methacrylate-acrylonitrile-butadiene-styrene (MABS), acrylate-styrene-acrylonitrile (ASA), all-acrylics, styrene-acrylonitrile grafted onto elastomeric backbones of ethylene-propylene-diene-monomer (SA EPDM), and methacrylic-acrylic rubber-styrene (MAS). More-preferred graft co-polymer resins are selected from the group consisting of MABS, ASA, all-acrylic and MBS. Most-preferred graft co-polymer resins are selected from the group consisting of MABS and ASA.

The ABS graft co-polymer resin preferably has a styrene-butadiene rubber core and a styrene-acrylonitrile shell.

The MBS graft co-polymer resin preferably has a styrene-butadiene rubber core and a shell of acrylic polymer or co-polymer.

The MABS graft co-polymer resin preferably has a styrene-butadiene rubber core and a shell of methacrylate-acrylonitrile co-polymer. More preferably, the MABS graft co-polymer resin has a core, which is approximately 75% by weight of the total weight thereof, which consists of butadiene and styrene in the weight ratio of about 50:25, and a shell of methyl methacrylate and acrylonitrile in the weight ratio of about 20:5.

The preferred ASA graft co-polymer resin is substantially as disclosed in US-A-3,944,631; accordingly unlike the remainder of the above-described graft co-polymer resins, the preferred ASA graft co-polymer resin contained relatively little grafting (column 1, lines 31-32 in connection with column 8, lines 9-45 and column 9, lines 1-20). A most-preferred ASA graft co-polymer resin, marketed under the trademark "SCC 1015" (see Table II below), is substantially as described in the '631 patent and includes a crosslinked acrylate elastomer, a crosslinked styrene-acrylonitrile co-polymer and a linear styrene-acrylonitrile co-polymer. The most-preferred ASA graft co-polymer resin, moreover, appears morphologically to be made of interpenetrating polymer networks.

Preferred all-acrylic graft copolymer resins are as disclosed in US-A-3,985,703.

Examples of commercially-available graft copolymer resins, of the types discussed above, are given in Table II.

The particularly preferred all-acrylic graft copolymer resins, marketed under the Trade Marks "KM 323 B" and "KM 330" (see Table II), have a rubber-type core, comprising approximately 75% of the total weight, which consists of butyl methacrylate-type monomers, and a shell of methyl methacrylate.

MABS resin "Blendex 452" (see Table II) is especially preferred; its properties are:

	Tensile strength	5516 kPa at 23°C (D-638-71; 0.085 mm/sec)
5	Tensile modulus	275800 kPa at 23°C (D-638-71)
	Heat deflection (annealed)	0.25 mm deflection at 48°C under a load of 1820 kPa (D-648-72)
10	Specific gravity	1.01 at 23°C (D-792-66, Method A-1)
	Hardness D	60 at 23°C (D-530, Type D, Method A)
	Izod impact (6.3 mm)	0.29 J/mm at 23°C (D-256-72, Method A)
15	Bulk density	25.6 kg/m ³ .

TABLE II

	Type of graft co-polymer resin	Trademark	Manufacturer
20	ABS	Abson 120	Mobay Chemical Co. Penn Lincoln Parkway West Pittsburgh, PA 15205
		Abson 161	"
25		Abson 171	"
		XP90030.01	The Dow Chemical Co. Midland, MI 48640
		XP74027.00	"
	MBS	KM 611	Rohm & Haas Co. Independence Mall West Philadelphia, PA 19105
		KM 608A	"
35		KM 653	"
		KM 641	"
		KM BTA-IIIS	"
		KM BTA-IIIF	"
		8003 B-X P	The Dow Chemical Co.
40	MABS	Acryloid KM 452 Blendex 452	Rohm & Haas Co. Borg-Warner Chemicals, Inc. Technical Centre Washington, WV 26181
45	ASA	SCC 1015	Stauffer Chemical Co. 299 Park Ave. New York, NY 10017
	All-acrylic	KM 323B KM 330	Rohm & Haas Co. "
50	SA EPDM	Rovel	Uniroyal Chemical Division of Uniroyal, Inc. Naugatuck, CT 06770
55	MAS	Vitax	Hitachi, Ltd. Tokyo, Japan

Experimental procedure

Unless indicated otherwise, adhesive compositions were prepared by combining two separate (i.e., distinct) mixtures of methyl methacrylate ester monomer. One of the two monomer mixtures contained the chlorosulfonated polyethylene resin. The other of the monomer mixtures contained the graft co-polymer resin. The mixtures were independently (i.e., separately) mixed, preferably using a "Hobart" mixer, and thereafter blended together, preferably using a "Hockmeyer" high-speed dispersion apparatus, to make the adhesive compositions disclosed below.

Adhesive strength (i.e., compression shear) of bonds, as between plastic materials, formed from such

adhesive compositions were measured using a modification of a test outlined in ASTM D905-49. To test compression shear strength, for example, adhesive-bond test specimens consisted of a first 25 mm×25 mm×6.3 mm plastic coupon bonded to a second 25 mm×50 mm×6.3 mm plastic coupon, substantially in accordance with the ASTM D905-49 test method mentioned above. The area of each coupon to be bonded was coated with a surface activator, such as, for example, the well-known condensation product of butyraldehyde and aniline discussed above. The surface activator, currently being sold commercially under the trademark "Vanax 808", moreover, included about 0.1 weight percent of copper naphthanate which had been added thereto. Then an effective amount of adhesive composition for substantially covering the area to be bonded was applied to one of the coupons, and the two coupons were thereafter pressed together. A 0.25 mm metal shim washer was used to measure (or gauge) the bond thicknesses. After conditioning for two days at room temperature (as used herein, "room temperature" is defined to be 25 degrees Centigrade), the coupons were thereafter tested in compression shear (substantially as specified in ASTM D905-49) using a crosshead speed of 1.27 mm per minute.

Adhesive shear strength of adhesive bonds formed between cold-rolled steel coupons were tested, in accordance with the test method of ASTM D-1002-64, using like pairs of 25 mm×76 mm×1.6 mm coupons. Such coupons were first washed with methyl ethyl ketone (MEK), grit blasted, and thereafter re-washed with MEK prior to being tested. Coupon surfaces were preferably coated with the butyraldehyde-aniline condensation-product surface activator (discussed immediately above), and thereafter had the adhesive composition applied thereto, also generally as described above, except that a mold was used to index the coupons to provide uniform bonds having an area of about 12.5 mm×25 mm and a thickness of about 0.2 mm. Such bonds were conditioned for two days at room temperature, and thereafter tested at a separation rate of 1.27 mm per minute.

Peel strength of the adhesive compositions were tested according to the test method of ASTM D-1876-61T, using a pair of like 25 mm×254 mm×0.5 mm cold-rolled steel coupons. The coupons were first washed with MEK, abraded with sandpaper, and thereafter re-cleaned with MEK. Approximately 23 cm (9 inches) of the length of one such coupon was bonded to approximately 23 cm (9 inches) of the length of the other coupon, using the activation and application technique described immediately above, except that 0.18 mm wire spacers were used to measure (or gauge) bond thicknesses as the coupons were pressed together with weights in accordance with the testing method of ASTM D-1876-61T. After conditioning for two days at room temperature, the samples were tested in 180 degree peel at a rate of 254 mm per minute.

Impact strength of the adhesive compositions disclosed below were tested generally according to ASTM D950-54, except that 12.7 mm (in diameter) steel bars (or rods) having lengths of 76.2 mm and 9.5 mm respectively were used instead of test specimens having dimensions specified in the testing method of ASTM D950-54. Surfaces to be bonded together were first solvent cleaned, then grit blasted, then activated, then bonded together, and thereafter conditioned for two days at room temperature prior to testing.

For the adhesive compositions disclosed below, a cure time of from about 6 to about 8 hours resulted in achieving approximately 80% or more of ultimate bond strength.

In the following Tables III to X, various examples of adhesive compositions are presented. All amounts are given in parts by weight. The following abbreviations are used:

- CSPE1=chlorosulfonated polyethylene resin (Hypalon 30)
- CSPE2=chlorosulfonated polyethylene resin (Hypalon 20)
- CSPE3=chlorosulfonated polyethylene resin (Hypalon LD-999)
- CSPE4=chlorosulfonated polyethylene resin (Hypalon 485)
- MMA=methyl methacrylate monomer
- CHP=cumene hydroperoxide
- MAcid=methacrylic acid
- MABS1=MABS graft copolymer resin (Blendex 452)
- MABS2=MABS graft copolymer resin (Acryloid KM 452)
- pTSC=p-toluenesulfonyl chloride
- PSC=propanesulfonyl chloride
- ASA=ASA graft copolymer resin (SCC 1015)
- AllA1=All-Acrylic graft copolymer resin (KM 323 B)
- AllA2=All-Acrylic graft copolymer resin (KM 330)
- MBS1=MBS graft copolymer resin (KM 608A)
- MBS2=MBS graft copolymer resin (KM 611)
- MBS3=MBS graft copolymer resin (KM 641)
- MBS4=MBS graft copolymer resin (KM 653)
- MBS5=MBS graft copolymer resin (8003 B-X P).

Examples 1 to 5 contain varying ratios of chlorosulfonated polyethylene polymer to MABS graft copolymer (the figure of 103 in Example 5 is based on 34.5% MABS1 in MMA). The same is true of Examples 6 to 12, but at a substantially constant chlorosulfonated polyethylene polymer plus graft copolymer solids level, so as to separate out effects which might otherwise be caused by variation of this solids level. In Examples 5 and 7 to 12, pTSC/PSC is added to activate cure in the absence of sulfonyl chloride moiety, a function usually provided by the CSPE resin.

Examples 13 to 18 are not tabulated. They are repeats of Example 3, except that the percentage of

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MABS1 in the monomer was respectively 25, 25, 27, 24, 19 and 25, and the monomer was respectively methyl, ethyl, butyl, cyclohexyl, 2-ethylhexyl and tetrahydrofuryl methacrylate.

Examples 19 to 23 contain various ratios of chlorosulfonated polyethylene polymer to ASA graft copolymer. In Example 23, pTSC is added for the same reason as in Example 5.

Examples 24 to 29 contain varying ratios of chlorosulfonated polyethylene polymer to All-Acrylic graft copolymer.

Examples 30 to 44 contain varying ratios of chlorosulfonated polyethylene polymer to MBS graft copolymer. MBS3 has a smaller particle size than MBS2 which itself has a smaller particle size than MBS4.

Examples 45 to 49 (comparative) contain either a chlorosulfonated polyethylene polymer or a graft copolymer, but not both.

Examples 50 to 53 containing varying amounts of methacrylic acid, while the amounts of the remaining components were held substantially constant. Examples 54 to 56 contain three different varieties of chlorosulfonated polyethylene in combination with MABS graft copolymer.

TABLE III

	1	2	Example 3	4	5
40% CSPE1 in MMA	100	75	50	25	0
25% MABS1 in MMA	0	25	50	75	103
MAcid	5	5	5	5	5
CHP	0.5	0.5	0.5	0.5	0.5
pTSC	0	0	0	0	1.26
CSPE1+MABS1	40	36.25	32.5	28.75	35.5
CSPE1:MABS1	—	30:6.25	20:12.5	10:18.75	—

TABLE IV

	6	7	8	Example 9	10	11	12
CSPE1	34.8	27.8	20.9	17.4	13.9	7.0	0
MABS1	0	7.0	13.9	17.4	20.9	27.8	34.8
MMA	65.2	65.2	65.2	65.2	65.2	65.2	65.2
MAcid	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CHP	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PSC	0	0.34	0.67	0.84	1.01	1.35	1.69
CSPE1+MABS1	34.8	34.8	34.8	34.8	34.8	34.8	34.8
CSPE1:MABS1	—	27.8:7.0	20.9:13.9	17.4:17.4	13.9:20.9	7.0:27.8	—

TABLE V

		19	20	Example 21	22	23
5	40% CSPE1 in MMA	100	75	50	25	0
	22.5% ASA in MMA	0	25	50	75	100
10	MAcid	5	5	5	5	5
	CHP	0.5	0.5	0.5	0.5	0.5
	pTSC	0	0	0	0	1.26
15	CSPE1+ASA	40	35.63	31.25	26.88	22.5
	CSPE1:ASA	40:0	30:5.63	20:11.25	10:16.88	0:22.5

TABLE VI

		24	25	26	Example 27	28	29
25	40% CSPE1 in MMA	75	50	25	75	50	25
	17.5% AIIA1 in MMA	25	50	75	—	—	—
	18.1% AIIA2 in MMA	—	—	—	25	50	75
30	MAcid	5	5	5	5	5	5
	CHP	0.5	0.5	0.5	0.5	0.5	0.5
35	CSPE1+AIIA	34.38	28.75	23.13	34.53	29.05	23.58
	CSPE1:AIIA	30:4.38	20:8.75	10:13.13	30:4.53	20:9.05	10:13.58

TABLE VII

	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
40% CSPE1 in MMA	75	50	25	75	50	25	75	50	25	75	50	25	75	50	25
32.25% MBS1 in MMA	25	50	75	—	—	—	—	—	—	—	—	—	—	—	—
31.8% MBS2 in MMA	—	—	—	25	50	75	—	—	—	—	—	—	—	—	—
35% MBS3 in MMA	—	—	—	—	—	—	25	50	75	—	—	—	—	—	—
24.1% MBS4 in MMA	—	—	—	—	—	—	—	—	—	25	50	75	—	—	—
19.6% MBS5 in MM	—	—	—	—	—	—	—	—	—	—	—	—	25	50	75
MAcid	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
CHP	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
CSPE1+MBS	38.13	36.25	34.38	37.95	35.90	33.85	38.75	37.50	36.25	36.03	32.05	28.08	34.90	29.80	24.70
CSPE1:MBS	30: 8.13	20: 16.25	10: 24.38	30: 7.95	20: 15.90	10: 23.85	30: 8.75	20: 17.50	10: 26.25	30: 6.03	20: 12.05	10: 18.08	30: 4.90	20: 9.80	10: 14.70

TABLE VIII

		45	46	Example 47	48	49
5	CSPE1	40	—	—	—	—
	MBS4	—	33.5	—	—	—
10	MBS2	—	—	33.5	—	—
	MBS5	—	—	—	33.5	—
	AlIA1	—	—	—	—	21.5
15	MMA	60	66.5	66.5	66.5	78.5
	MAcid	5	5	5	5	5
20	CHP	0.5	0.5	0.5	0.5	0.5
	pTSC	—	5	5	5	5

TABLE IX

		50	Example 51	52	53
25	CSPE1	20	20	20	20
30	MABS1	12.5	12.5	12.5	12.5
	MMA	67.5	67.5	67.5	67.5
35	MAcid	15	10	5	0
	CHP	0.5	0.5	0.5	0.5
40	Ionol	0.25	0.25	0.25	0.25

TABLE X

		54	Example 55	56
45	40% CSPE2 in MMA	50	—	—
	40% CSPE3 in MMA	—	50	—
	40% CSPE4 in MMA	—	—	50
50	25% MABS1 in MMA	50	50	50
	MAcid	5	5	5
55	CHP	0.5	0.5	0.5

For the adhesive compositions of the instant invention, polymerization of the acrylate-based (preferably methacrylate-based) ester and acid monomers thereof causes the composition to set up, harden, and cure. The catalyst "triggers" the polymerization steps. The activator (or initiator) when included, in turn, triggers the catalyzation step.

In a first preferred method of practicing the present invention, the adhesive composition, excluding the activator (or initiator), is applied to at least a first one of at least two surfaces which are to be bonded together. The activator is applied to the other surface. The two surfaces are then brought into such close proximity that the activator contacts the adhesive composition, whereby the activator triggers catalytic action of the catalyst. Such action by the catalyst, in turn, initiates polymerization of the monomers,

whereby the composition is caused to set up, harden and cure. Such an application or method of use is generally referred to as a one-part adhesive because only a relatively small amount of activator (relative to the amount of total adhesive composition) is needed to trigger the action of the catalyst.

A second preferred method of practicing the present invention is via the combination or mixture of both parts of a so-called two-part adhesive. The two-part adhesive comprises first and second portions of the adhesive composition. The first portion includes some of the adhesive composition ingredients and the catalyst. The second portion includes the remainder of the adhesive composition components and the activator.

The two portions are generally mixed in a ratio of from 5:95 to 95:5 v/v; 1:1 v/v is often preferred. Regardless of the mixing ratio, the relative proportions of the catalyst and activator (or initiator) must be selected so that effective polymerisation results. Example 57 (not tabulated) is of two parts. Part A comprises 35.5 parts CSPE1, 53.2 parts MMA, 9.8 parts methacrylic acid, 1.0 part CHP and 0.5 part Ionol (a stabiliser which serves to avoid premature gelation of the graft copolymer); part B comprises 25.0 parts MABS2, 75.0 parts MMA, 4.995 parts of a first initiator (Vanax 808) and 0.005 part of a second initiator which is a copper naphthanate solution sold commercially by Tenneco Chemicals, Inc., Heyden Division, 280 Park Avenue, New York, N.Y. 10017, USA, under the Nuodex Trade Mark. When approximately 5 grams of each of parts A and B were mixed together, the adhesive composition had a working time (i.e. the time during which the composition is generally acknowledged to be substantially workable or fluid-like) of about 2 minutes. The adhesive composition began to thicken or gel about 2.5 minutes after mixing, exhibited a definite exotherm during mixing and hardening, and hardened about 5 minutes after mixing. Larger quantities may be expected to harden in less time, and exhibit a more pronounced exotherm.

The properties of the compositions of Examples 1 to 57 are given in the following Table XI. In this Table: "Comp. (ABS)", "Comp. (PVC)" and "Comp. (PMA)" refer to the compression shear strengths for ABS, polyvinyl chloride and polymethyl methacrylate coupons, respectively. "Lap" refers to the lap shear strength for steel coupons. "Peel" refers to the peel strength and "impact" refers to the impact strength.

The viscosity values are Brookfield viscosities, measured using a number 3 spindle and 10 rpm for Examples 1 and 2, number 4/10 rpm for Example 3, "TB"/10 rpm for Example 4, "TF"/10 rpm for Example 5, number 2/20 rpm for Example 6, "TA"/20 rpm for Examples 7 and 8, and "TC"/10 rpm for Examples 9 to 12.

"nt"=not tested.

"cpf"=coupon failed.

For Examples 6 to 11, the ABS and PVC coupons failed at the given values. For Examples 15 and 17, a saw-tooth pattern was recorded, i.e. the bond slips and grabs.

TABLE XI

Example units	Comp. ABS kPa (psi)	Comp. PVC kPa (psi)	Comp. PMA kPa (psi)	Lap shear kPa (psi)	Peel J/mm (pli)	Impact kJ/m ² (ft-lb/in ²)	Viscosity mPa . s (cp)
1	8930 (1295)	11240 (1630)	8240 (1195)	21920 (3180)	3.9 (22.5)	33.0 (15.7)	8800
2	9690 (1405)	14500 (2175)	10170 (1475)	nt	4.7 (27)	nt	14800
3	10310 (1495)	16550 (2400)	18790 (2725)	29650 (4300)	5.0 (29)	43.0 (20.3)	25600
4	7380 (1070)	12310 (1785)	14100 (2045)	nt	4.6 (26.5)	nt	36800
5	7760 (1125)	12170 (1765)	13790 (2000)	11070 (1605)	6.1 (35)	47.5 (22.6)	124000
6	7930 (1550)	15170 (2200)	18270 (2650)	21550 (3125)	4.8 (27.5)	36.5 (17.4)	2240
7	10520 (1525)	13790 (2000)	18960 (2750)	29480 (4275)	6.1 (35)	47.2 (22.5)	7200
8	9310 (1350)	13790 (2000)	18270 (2650)	29130 (4225)	6.8 (39)	48.7 (23.2)	43200
9	8620 (1250)	13100 (1900)	15520 (2250)	28200 (4090)	6.6 (38)	52.0 (24.8)	92000
10	9310 (1350)	12760 (1850)	16380 (2375)	26680 (3870)	6.7 (38.5)	43.8 (20.9)	120000
11	8450 (1225)	13100 (1900)	10520 (1525)	25790 (3740)	6.0 (34.5)	44.3 (21.1)	208000
12	8280 (1200)	10520 (1525)	nil	21930 (3180)	5.3 (30)	38.4 (18.3)	264000

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TABLE XI (continued)

Example units	Comp. ABS kPa (psi)	Comp. PVC kPa (psi)	Comp. PMA kPa (psi)	Lap shear kPa (psi)	Peel J/mm (pli)	Impact kJ/m ² (ft-lb/in ²)
13	8550 (1240)	cpf	21650 (3140)	25790 (3740)	6.0 (34)	42.0 (20)
14	8790 (1275)	cpf	10450 (1515)	23270 (3375)	5.8 (33)	33.6 (16)
15	3720 (540)	12030 (1745)	9270 (1345)	17650 (2560)	1.3 (7.25)	25.2 (12)
16	690 (100)	3520 (510)	1380 (200)	9650 (1400)	0.2 (1)	10.5 (5)
17	3620 (525)	4070 (590)	5030 (730)	7760 (1125)	0.9 (5.15)	6.3 (3)
18	3760 (545)	5170 (750)	4550 (660)	21170 (3070)	0.5 (3)	10.5 (5)
19	10690 (1550)	cpf	20860 (3025)	23680 (3420)	2.6 (15)	34.6 (16.5)
20	7340 (1065)	cpf	13100 (1900)	30340 (4400)	4.2 (24)	nt
21	7580 (1100)	14130 (2050)	12930 (1875)	29580 (4290)	4.7 (27)	31.5 (15)
22	3280 (475)	11310 (1640)	12760 (1850)	29580 (4290)	4.4 (25)	nt
23	9760 (1415)	cpf	11720 (1700)	27790 (4030)	1.7 (10)	29.4 (14)
24	8960 (1300)	13790 (2000)	15000 (2175)	28340 (4110)	5.2 (30)	26.7 (12.7)
25	9140 (1325)	11890 (1725)	23790 (3450)	28960 (4200)	3.1 (18)	22.3 (10.6)
26	6030 (875)	8270 (1200)	17410 (2525)	24890 (3610)	2.3 (13)	19.3 (9.2)
27	5690 (825)	cpf	13030 (1890)	28790 (4175)	5.4 (31)	nt
28	7240 (1050)	cpf	14580 (2115)	28200 (4090)	5.6 (32)	nt

TABLE XI (continued)

Example units	Comp. ABS kPa (psi)	Comp. PVC kPa (psi)	Comp. PMA kPa (psi)	Lap shear kPa (psi)	Peel J/mm (pli)	Impact kJ/m ² (ft-lb/in ²)
29	4650 (675)	9310 (1350)	9680 (1390)	25720 (3730)	5.8 (33)	nt
30	nt	nt	nt	28030 (4065)	nt	nt
31	2070 (300)	8620 (1250)	8270 (1200)	27440 (3980)	4.5 (26)	31.5 (15)
32	nt	nt	nt	8210 (1190)	nt	nt
33	nt	nt	nt	29720 (4310)	nt	nt
34	5340 (775)	7070 (1025)	15170 (2200)	28440 (4125)	5.2 (30)	40.7 (19.4)
35	nt	nt	nt	24480 (3550)	nt	nt
36	nt	nt	nt	29100 (4220)	nt	nt
37	2420 (350)	7410 (1075)	9480 (1375)	25240 (3660)	2.6 (15)	25.8 (12.3)
38	nt	nt	nt	18340 (2660)	nt	nt
39	6720 (975)	cpf	8720 (1265)	28990 (4205)	6.6 (38)	nt
40	2520 (365)	8960 (1300)	7070 (1025)	24270 (3520)	2.6 (15)	nt
41	2860 (415)	7070 (1025)	17070 (2475)	nil	nil	nt
42	4480 (650)	cpf	8380 (1215)	29060 (4215)	6.6 (38)	nt
43	2240 (325)	9140 (1325)	6480 (940)	24930 (3615)	7.1 (41)	nt
44	1480 (215)	7240 (1050)	8450 (1225)	23620 (3425)	6.4 (36.5)	nt

TABLE XI (continued)

Example units	Comp. ABS kPa (psi)	Comp. PVC kPa (psi)	Comp. PMA kPa (psi)	Lap shear kPa (psi)	Peel J/mm (pli)	Impact kJ/m ² (ft-lb/in ²)
45	10000 (1450)	—	13100 (1900)	23170 (3360)	3.3 (19)	28.3 (13.5)
46	4790 (695)	8830 (1280)	4100 (595)	620 (90)	0.2 (1)	2.1 (1.0)
47	4280 (620)	3620 (525)	4380 (635)	241 (35)	0.3 (2)	2.7 (1.3)
48	2590 (375)	5590 (810)	5010 (725)	4000 (580)	1.2 (7)	1.8 (0.9)
49	4760 (690)	6860 (995)	2590 (375)	1100 (160)	0.2 (1)	6.3 (3.0)
50	—	—	—	32060 (4650)	—	—
51	—	—	—	31370 (4550)	—	—
52	—	—	—	30680 (4450)	—	—
53	—	—	—	15860 (2300)	—	—
54	8790 (1275)	9650 (1400)	22240 (3225)	25550 (3705)	5.8 (33)	43.0 (20.5)
55	7930 (1150)	10000 (1450)	20340 (2950)	25550 (3705)	5.2 (30)	44.7 (21.3)
56	nt	nt	nt	28240 (4095)	5.8 (33)	48.1 (22.9)
57	10410 (1510)	18000 (2610)	28960 (4200)	27300 (3960)	—	47.5 (22.6)

For example, in addition to having usefulness in the area of adhesives, it is contemplated that the present invention is generally useful in the areas of repair products, casting materials and coatings. In the repair-products field, for example, a piece of fiberglass cloth can be wetted on both sides with the present invention to make a fiberglass patch. It is further contemplated that the present invention can include an effective amount of metal particles for producing repair products having a variety of commercially desirable features.

Furthermore, in the casting-materials area, the present invention can be used as a carrier of preselected components much the way epoxies are currently used.

In the coatings field, for example, the present invention can be used to permanently coat metal substrates for a variety of reasons.

Claims

1. An adhesive composition comprising an acrylate-based or a methacrylate-based ester monomer; a catalyst; a chlorinated polyethylene plus an organic sulfonylchloride, or a chlorosulfonated polyethylene; and a graft copolymer resin in the form of particles having a rubber-like core and a relatively hard shell.
2. An adhesive composition according to claim 1, in which the ester monomer is selected from methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate and tetrahydrofurfuryl methacrylate.
3. An adhesive composition according to claim 1 or claim 2, in which the catalyst is a free-radical generator selected from organic peroxides, organic hydroperoxides, peresters and peracids.
4. An adhesive composition according to claim 3, in which the catalyst is cumene hydroperoxide.
5. An adhesive composition according to any preceding claim, in which the graft copolymer resin is selected from ABS, MBS, MABS, ASA, all-acrylic, SA, EPDM and MAS.
6. An adhesive composition according to any preceding claim, which additionally comprises an acrylate-based or a methacrylate-based acid monomer.
7. An adhesive composition according to claim 6, in which the acid monomer is methacrylic acid.
8. An adhesive composition according to any preceding claim, which comprises the chlorosulfonated polyethylene.
9. An adhesive composition according to claim 8, in which the chlorosulphonated polyethene contains about 43% by weight chlorine, about 1.1% by weight sulfur, and 34 millimoles of sulfonyl chloride moiety per 100 grams thereof.
10. An adhesive composition according to any of claims 1 to 7, which comprises the chlorinated polyethylene plus the organic sulfonyl chloride.
11. An adhesive composition according to claim 10, in which the organic sulfonyl chloride is propanesulfonyl chloride or para-toluenesulfonyl chloride.
12. An adhesive composition according to any of claims 8 to 11, which comprises an added catalyst activator.
13. An adhesive composition according to claim 12, in which the added catalyst activator is an aldehyde-amine condensation product.
14. A method of adhesively bonding two surfaces, which comprises applying to the first surface an adhesive composition according to any of claims 1 to 11 but free of catalyst activator, applying to the second surface a catalyst activator, and bringing the thus-treated surfaces into contact.
15. A method according to claim 14, in which the adhesive composition comprises an ester monomer as defined in claim 2 and a free-radical generating catalyst as defined in claim 3, and in which the catalyst activator is an aldehyde-amine condensation product or an organic sulfonyl chloride.
16. A method of adhesively bonding two surfaces, which comprises applying to the first surface an adhesive composition according to any of claims 1 to 11 but free of catalyst activator, applying to the second surface a composition according to any of claims 1 to 13 but free of catalyst, and bringing the thus-treated surfaces into contact.

Patentansprüche

1. Klebstoffzusammensetzung bestehend aus Estermonomeren auf Acrylat- oder Methacrylat-Basis; chloriertem Polyethylen in Verbindung mit organischem Sulfonylchlorid, oder chloresulfonyliertem Polyethylen; und einem partikelförmigem Harz mit einem gummiähnlichen Kernbereich und einer relativ harten Schale als Pfropf-Copolymer.
2. Klebstoffzusammensetzung nach Anspruch 1, bei der als Estermonomer Methyl-Methacrylat, Ethyl-Methacrylat, Butyl-Methacrylat, Cyclohexyl-Methacrylat, 2-Ethylhexyl-Methacrylat oder Tetrahydrofurfuryl-Methacrylat verwendet wird.
3. Klebstoffzusammensetzung nach einem der Ansprüche 1 oder 2, bei der der Katalysator eine freie Radikale erzeugende Verbindung aus der Gruppe der organischen Peroxide, organischen Hydroperoxide, Perester oder Persäuren ist.
4. Klebstoffzusammensetzung nach Anspruch 3, bei der der Katalysator Isopropylbenzolhydroperoxid ist.

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For example, in addition to having usefulness in the area of adhesives, it is contemplated that the present invention is generally useful in the areas of repair products, casting materials and coatings. In the repair-products field, for example, a piece of fiberglass cloth can be wetted on both sides with the present invention to make a fiberglass patch. It is further contemplated that the present invention can include an effective amount of metal particles for producing repair products having a variety of commercially desirable features.

Furthermore, in the casting-materials area, the present invention can be used as a carrier of preselected components much the way epoxies are currently used.

In the coatings field, for example, the present invention can be used to permanently coat metal substrates for a variety of reasons.

Claims

1. An adhesive composition comprising an acrylate-based or a methacrylate-based ester monomer; a catalyst; a chlorinated polyethylene plus an organic sulfonylchloride, or a chlorosulfonated polyethylene; and a graft copolymer resin in the form of particles having a rubber-like core and a relatively hard shell.
2. An adhesive composition according to claim 1, in which the ester monomer is selected from methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate and tetrahydrofurfuryl methacrylate.
3. An adhesive composition according to claim 1 or claim 2, in which the catalyst is a free-radical generator selected from organic peroxides, organic hydroperoxides, peresters and peracids.
4. An adhesive composition according to claim 3, in which the catalyst is cumene hydroperoxide.
5. An adhesive composition according to any preceding claim, in which the graft copolymer resin is selected from ABS, MBS, MABS, ASA, all-acrylic, SA, EPDM and MAS.
6. An adhesive composition according to any preceding claim, which additionally comprises an acrylate-based or a methacrylate-based acid monomer.
7. An adhesive composition according to claim 6, in which the acid monomer is methacrylic acid.
8. An adhesive composition according to any preceding claim, which comprises the chlorosulfonated polyethylene.
9. An adhesive composition according to claim 8, in which the chlorosulphonated polyethene contains about 43% by weight chlorine, about 1.1% by weight sulfur, and 34 millimoles of sulfonyl chloride moiety per 100 grams thereof.
10. An adhesive composition according to any of claims 1 to 7, which comprises the chlorinated polyethylene plus the organic sulfonyl chloride.
11. An adhesive composition according to claim 10, in which the organic sulfonyl chloride is propanesulfonyl chloride or para-toluenesulfonyl chloride.
12. An adhesive composition according to any of claims 8 to 11, which comprises an added catalyst activator.
13. An adhesive composition according to claim 12, in which the added catalyst activator is an aldehyde-amine condensation product.
14. A method of adhesively bonding two surfaces, which comprises applying to the first surface an adhesive composition according to any of claims 1 to 11 but free of catalyst activator, applying to the second surface a catalyst activator, and bringing the thus-treated surfaces into contact.
15. A method according to claim 14, in which the adhesive composition comprises an ester monomer as defined in claim 2 and a free-radical generating catalyst as defined in claim 3, and in which the catalyst activator is an aldehyde-amine condensation product or an organic sulfonyl chloride.
16. A method of adhesively bonding two surfaces, which comprises applying to the first surface an adhesive composition according to any of claims 1 to 11 but free of catalyst activator, applying to the second surface a composition according to any of claims 1 to 13 but free of catalyst, and bringing the thus-treated surfaces into contact.

Patentansprüche

1. Klebstoffzusammensetzung bestehend aus Estermonomeren auf Acrylat- oder Methacrylat-Basis; chloriertem Polyethylen in Verbindung mit organischem Sulfonylchlorid, oder chloresulfoniertem Polyethylen; und einem partikelförmigem Harz mit einem gummiähnlichen Kernbereich und einer relativ harten Schale als Pflropf-Copolymer.
2. Klebstoffzusammensetzung nach Anspruch 1, bei der als Estermonomer Methyl-Methacrylat, Ethyl-Methacrylat, Butyl-Methacrylat, Cyclohexyl-Methacrylat, 2-Ethylhexyl-Methacrylat oder Tetrahydrofurfuryl-Methacrylat verwendet wird.
3. Klebstoffzusammensetzung nach einem der Ansprüche 1 oder 2, bei der der Katalysator eine freie Radikale erzeugende Verbindung aus der Gruppe der organischen Peroxide, organischen Hydroperoxide, Perester oder Persäuren ist.
4. Klebstoffzusammensetzung nach Anspruch 3, bei der der Katalysator Isopropylbenzohydroperoxid ist.



5. Klebstoffzusammensetzung nach einem der vorhergehenden Ansprüche, bei der als Pfropf-Copolymer folgende Substanzen verwendet werden können: ABS, MSB, Methacrylat-Acrylnitril-Butadien-Styrol, Acrylat-Acrylnitril-Styrol, alle Acryle, Acrylnitril-Styrol, EPDM oder Methacrylat-Acrylat-Gummi-Styrol.

6. Klebstoffzusammensetzung nach einem der vorhergehenden Ansprüche, die zusätzlich ein Säuremonomer auf Acrylat- oder Methacrylat-Basis enthält.

7. Klebstoffzusammensetzung nach Anspruch 6, bei der das Säuremonomer Methacrylsäure ist.

8. Klebstoffzusammensetzung nach einem der vorhergehenden Ansprüche, welche das chloresulfonierte Polyethylen enthält.

9. Klebstoffzusammensetzung nach Anspruch 8, bei der 100 g des chloresulfonierten Polyethylens um die 43 g Chlor, ca. 1,1 g Schwefel und 34 Millimole Sulfonylchlorid enthalten.

10. Klebstoffzusammensetzung nach einem der Ansprüche 1 bis 7, die chloriertes Polyethylen und organisches Sulfonylchlorid enthält.

11. Klebstoffzusammensetzung nach Anspruch 10, bei der das organische Sulfonylchlorid Propan-sulfonylchlorid oder Para-Toluolsulfonylchlorid ist.

12. Klebstoffzusammensetzung nach einem der Ansprüche 8 bis 11, die einen zugesetzten Aktivator für den Katalysator enthält.

13. Klebstoffzusammensetzung nach Anspruch 12, bei der der zugesetzte Katalysator-Aktivator ein Kondensationsprodukt aus einem Aldehyd und einem Amin.

14. Verfahren zur Verbindung zweier Flächen mittels Klebstoff, bei dem die erste Fläche mit einer Klebstoffzusammensetzung nach einem der Ansprüche 1 bis 11 versehen wird, die keinen Katalysator-Aktivator enthält, auf die zweite Fläche ein Katalysator-Aktivator aufgetragen wird und die so behandelten Flächen in Kontakt zueinander gebracht werden.

15. Verfahren nach Anspruch 14, bei dem die Klebstoffzusammensetzung ein Estermonomer gemäß Anspruch 2 und einen freie Radikale erzeugenden Katalysator gemäß Anspruch 3 enthält und bei der der Katalysator-Aktivator ein Kondensationsprodukt aus einem Aldehyd und einem Amin oder ein organisches Sulfonylchlorid ist.

16. Verfahren zur Verbindung zweier Flächen mittels Klebstoff, bei dem die erste Fläche mit einer Klebstoffzusammensetzung gemäß einem der Ansprüche 1 bis 11 versehen wird, wobei die besagte Klebstoffzusammensetzung keinen Katalysator-Aktivator enthält, die zweite Fläche mit einer katalysatorfreien Zusammensetzung nach einem der Ansprüche 1 bis 13 versehen wird und die so behandelten Flächen in Kontakt zueinander gebracht werden.

Revendications

1. Composition adhésive, comprenant comme monomère un ester à base d'acrylate ou un ester à base de méthacrylate; un catalyseur; un polyéthylène chloré plus un chlorure de sulfonyle organique, ou un polyéthylène chlorosulfoné; et une résine du type copolymère greffé sous la forme de particules ayant un noyau semblable au caoutchouc et une enveloppe relativement dure.

2. Composition adhésive suivant la revendication 1, dans laquelle l'ester monomère est choisi entre le méthacrylate de méthyle, le méthacrylate d'éthyle, le méthacrylate de butyle, le méthacrylate de cyclohexyle, le méthacrylate de 2-éthylhexyle et le méthacrylate de tétrahydrofurfuryle.

3. Composition adhésive suivant la revendication 1 ou la revendication 2, dans laquelle le catalyseur est un générateur de radicaux libres choisi entre des peroxydes organiques, des hydroperoxydes organiques, des peresters et des peracides.

4. Composition adhésive suivant la revendication 3, dans laquelle le catalyseur est l'hydroperoxyde de cumène.

5. Composition adhésive suivant l'une quelconque des revendications précédentes, dans laquelle la résine du type copolymère greffé est choisie entre des résines ABS, MBS, MABS, ASA, des résines entièrement acryliques, des résines SA, EPDM et MAS.

6. Composition adhésive suivant l'une quelconque des revendications précédentes, qui comprend en outre comme monomère un acide à base d'acrylate ou à base de méthacrylate.

7. Composition adhésive suivant la revendication 6, dans laquelle le monomère acide est l'acide méthacrylique.

8. Composition adhésive suivant l'une quelconque des revendications précédentes, qui comprend le polyéthylène chlorosulfoné.

9. Composition adhésive suivant la revendication 8, dans laquelle le polyéthylène chlorosulfoné contient environ 43% en poids de chlore, environ 1,1% en poids de soufre et 34 millimoles de groupement chlorure de sulfonyle pour 100 grammes de produit.

10. Composition adhésive suivant l'une quelconque des revendications 1 à 7, qui comprend le polyéthylène chloré plus le chlorure de sulfonyle organique.

11. Composition adhésive suivant la revendication 10, dans laquelle le chlorure de sulfonyle organique est le chlorure de propanesulfonyle ou le chlorure de paratoluènesulfonyle.

12. Composition adhésive suivant l'une quelconque des revendications 8 à 11, qui est additionnée d'un activateur de catalyseur.



13. Composition adhésive suivant la revendication 12, dans laquelle l'activateur de catalyseur ajouté est un produit de condensation aldéhyde-amine.

14. Procédé pour produire la liaison d'adhérence entre deux surfaces, qui consiste à appliquer à la première surface une composition adhésive suivant l'une quelconque des revendications 1 à 11, mais
5 dépourvue d'activateur de catalyseur, à appliquer à la seconde surface un activateur de catalyseur et à mettre en contact l'une avec l'autre les surfaces ainsi traitées.

15. Procédé suivant la revendication 14, dans lequel la composition adhésive comprend un ester monomère tel que défini dans la revendication 2 et un catalyseur engendrant des radicaux libres tel que défini dans la revendication 3, et dans lequel l'activateur de catalyseur est un produit de condensation
10 aldéhyde-aminé ou un chlorure de sulfonyle organique.

16. Procédé pour produire une liaison d'adhérence entre deux surfaces, qui consiste à appliquer à la première surface une composition adhésive suivant l'une quelconque des revendications 1 à 11, mais dépourvue d'activateur de catalyseur, à appliquer à la seconde surface une composition suivant l'une
15 l'autre les surfaces ainsi traitées.

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