

Description

The present invention relates to a vinyl chloride resin composition, and more particularly to a vinyl chloride resin composition having an improved impact resistance with an excellent transparency that the vinyl chloride resin itself possesses originally.

A so-called MBS resin wherein methyl methacrylate, styrene and the like are graft-polymerized onto a butadiene rubber has been used as a reinforcing agent for improving the impact resistance of vinyl chloride resins. It is important that the transparency of the resins is not impaired by the incorporation of the reinforcing agent. Various improvements of the reinforcing agent for vinyl chloride resins or of the process for improving the impact resistance of vinyl chloride resins without impairing the transparency of the resins are also proposed, for instance, as disclosed in Japanese Patent Publication Kokai No. 59-221317. However, demand for improvement of the quality of vinyl chloride resin products is still strong and a further improvement is desired.

As a means for markedly increasing the impact resistance imparting ability of the MBS reinforcing agent for vinyl chloride resins, it is well known to increase the butadiene content of the reinforcing agent. For this purposes, it has been attempted to increase the proportion of the rubber component in the reinforcing agent or to increase the butadiene content in the rubber component. However, the former means, namely the increase of the proportion of the rubber, causes a serious problem that since the graft copolymer changes into a massive material during the preparation thereof when the proportion of the rubber component exceeds about 65 % by weight, no satisfactory polymer powder is obtained and moreover the incorporation of the produced graft copolymer into vinyl chloride resins lowers the transparency of molded end products. The latter means, namely the increase of the butadiene content in the rubber component, also causes a serious problem that the transparency of molded end products is markedly lowered. Owing to such problems, there has not been provided a reinforcing agent having a butadiene content of not less than 60 % by weight which can impart a high impact resistance to vinyl chloride resins without impairing the high transparency of the resins.

GB-A-1 175 118 discloses a vinyl chloride resin composition comprising a vinyl chloride resin containing at least 70% by weight of vinyl chloride, and 1-50 percent by weight of a graft polymer obtained by graft polymerizing a monomeric mixture of an aromatic vinyl, acrylonitrile and an acrylic acid alkyl ester having an alkyl group of 1 to 10 carbon atoms in an aqueous dispersion of a trunk copolymer consisting of butadiene, aromatic vinyl and acrylonitrile, at least 90 percent of the particles of the said trunk copolymer having a particle diameter between 200 and 800 Å.

GB-A-886 343 discloses an intimate blend of 10 to 99 parts by weight of a hard vinyl chloride polymer and, correspondingly, 90 to 1 parts by weight of a graft polymer obtainable by the emulsion polymerisation of 10 to 60 parts by weight of a mixture of 50 to 90% by weight of a monomeric monovinylidene aromatic hydrocarbon or halohydrocarbon and 50 to 10% by weight of monomeric acrylonitrile, methacrylonitrile or a mixture thereof in the presence of 100 parts by weight of a natural or synthetic rubbery conjugated diene hydrocarbon polymer having a second order transition temperature below 0° C.

DE-B-1 470 866 discloses thermoplastic molding materials consisting of a mixture of 60 to 90% by weight polyvinyl chloride and/or a copolymer containing more than 70% by weight vinylchloride units and less than 30% by weight units of other monomers and 40 to 10% by weight of a graft copolymer prepared by graft polymerising in an aqueous solution 80 to 30 parts of a monomer mixture consisting of acrylonitrile, vinyl aromatic compounds and methylmethacrylate to 20 to 70 parts of polybutadiene and/or a copolymer consisting of more than 70% by weight butadiene.

EP-A-0 232 139 discloses an impact modifier for polyvinyl chloride resins comprising a graft interpolymer which is a rubbery random copolymer of styrene and butadiene having grafted thereto an interpolymer of styrene, acrylonitrile and methylmethacrylate the ratio of styrene, acrylonitrile and methylmethacrylate being in a proportion such that the refractive index of the graft interpolymer is within the range of the refractive index of polyvinyl chloride resins.

It has been found that the problems of the lowering of transparency and the difficulty in powdering can be solved by and a high impact resistance can be achieved with the transparency being kept on a high level by skillfully combining the above-mentioned both means to improve the impact resistance imparting ability of the MBS reinforcing agent, namely the means according to the increase of the proportion of the rubber component in the reinforcing agent and the means according to the increase of the butadiene content in the rubber component.

In accordance with the present invention, there is provided a vinyl chloride resin composition which comprises:

A vinyl chloride resin composition which comprises:

(A) 3 to 30 parts by weight of a graft copolymer having a butadiene content of at least 60 % by weight prepared by reacting (i) 0.1 to 3 parts by weight of a crosslinking monomer and (ii) 0 to 3 parts by weight of at least one of alkyl acrylates and alkyl methacrylates in the presence of (b) 85 to 95 parts by weight of a butadiene polymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of other vinyl monomers copolymerizable therewith, and then subjecting the reaction product to emulsion polymerization with (a) 15 to 35 parts by weight of a monomer mixture of 50 to 95 % by weight of an aromatic vinyl monomer, 0.1 to 40 % by weight of a vinyl cyanide monomer and 0 to 40 % by weight of other vinyl monomers copolymerizable therewith, the total of said butadiene polymer (b) and said monomer mixture (a) being 100 parts by weight and the amounts of the components (i) and (ii) being based on 100 parts by weight of the total of the components (a) and (b), and
(B) 97 to 70 parts by weight of a vinyl chloride resin.

Treatment of the butadiene polymer with a cross-linking monomer prior to the graft polymerization is effective for preventing the produced graft copolymer from coagulating into a massive material, whereby the graft copolymer is obtained in a good powder form. Accordingly, in another embodiment of the present invention, a reinforcing agent for vinyl chloride resins is prepared by adding a cross-linking monomer with optionally an alkyl acrylate and/or an alkyl methacrylate to an aqueous latex of the butadiene polymer (b), reacting them and thereafter emulsion polymerizing the monomer mixture (a) in the aqueous latex, in which the cross-linking monomer and the alkyl (meth)acrylate are used in amounts of 0.1 to 3 parts by weight and 0 to 3 parts by weight, respectively, per 100 parts by weight of the total of the components (a) and (b).

The features of the present invention are summarized as follows:

- (1) In order to increase the butadiene content of the reinforcing agent, the proportion of the rubber component is greatly increased and moreover the butadiene content in the rubber component is increased, whereby it is intended to improve the impact resistance with keeping the transparency of vinyl chloride resins on a high level.
- (2) In order to prevent the lowering of the refractive index of the reinforcing agent owing to the increase of the butadiene content in the reinforcing agent, the proportion of the aromatic vinyl monomer in the graft component is greatly increased.
- (3) In order to prevent the lowering of physical properties resulting from the increase of the content of aromatic vinyl monomer in the grafting portion, and in order to eliminate the problem in powder formation, the vinyl cyanide is introduced into the grafting portion so as to raise the softening point of the produced graft copolymer.
- (4) Cross-linking monomers may be reacted with the butadiene polymer prior to the graft polymerization, as occasion demands, in order to prevent the produced graft copolymer particles from coagulating into a mass.

The butadiene polymer used in the present invention is prepared by polymerizing butadiene and optionally with at least one other vinyl monomer copolymerizable therewith, for example, in a known emulsion polymerization manner.

The copolymerizable other vinyl monomer is used when it is required to raise the refractive index of the produced butadiene polymer or to impart a cross-linked structure to the butadiene polymer. The kind and amount of the copolymerizable vinyl monomer to be used vary depending on the properties desired to improve and the degree of improvement. In general, from the viewpoint of effectively improving the desired properties, it is desirable to use the copolymerizable vinyl monomer so that its content in the produced butadiene polymer is from 0 to 18 % by weight.

Representative examples of the vinyl monomer copolymerizable with butadiene are, for instance, an aromatic vinyl compound such as styrene, a vinyl cyanide compound such as acrylonitrile, an alkyl acrylate having a C₁ to C₅ alkyl group such as ethyl acrylate or butyl acrylate, a crosslinking monomer such as divinyl benzene or monoethylene glycol dimethacrylate, and the like. The copolymerizable vinyl monomers used in the invention are not limited to those exemplified above. They are used alone or in admixture thereof.

Butadiene and the other vinyl monomers copolymerizable therewith are used in such amounts as producing the butadiene polymer containing 82 to 100 % by weight, preferably 85 to 99.5 % by weight, of butadiene and 18 to 0 % by weight, preferably 15 to 0.5 % by weight, of the other vinyl monomers. When the content of butadiene is less than 82 % by weight, the impact resistance of the obtained vinyl chloride resin composition is on the same level as that of conventional compositions and no improvement of the impact resistance is obtained.

The preparation of the butadiene polymer may be carried out by polymerizing the monomer or monomers in one stage, for instance, in a usual emulsion polymerization manner, but it is preferable from the viewpoint of transparency to conduct the polymerization in two stages wherein about 62 to 80 % by

weight of butadiene and 0 to 18 % by weight of the other vinyl monomers are polymerized and the residual butadiene is then polymerized.

The thus prepared butadiene homo- or copolymers have a butadiene content of 82 to 100 % by weight which is higher as compared with conventional MBS reinforcing agents.

The butadiene polymers are used usually in the form of an aqueous latex in the following step of graft polymerization. Prior to the graft polymerization, 0.1 to 3 parts by weight of a crosslinking monomer and 0 to 3 parts by weight of at least one of alkyl acrylates and methacrylates based on 100 parts by weight of the total of the butadiene polymer (b) and the graft component (a) may be reacted with the butadiene polymer in the aqueous latex of the butadiene polymer.

The crosslinking monomer serves to cause the graft component to polymerize on the surface of the butadiene polymer particles rather than inside the particles, thereby eliminating the problem encountered in the prior art that the graft copolymers are produced in a massive form and, therefore, no good powder is obtained. When the proportion of the butadiene polymer based on the total weight of the butadiene polymer and the graft component is over 70 % by weight, the crosslinking monomer is preferably used in an amount of 0.3 to 3 parts by weight.

In the treatment of the butadiene polymer with the crosslinking monomer, the alkyl acrylate and/or alkyl methacrylate are used optionally for the purpose of fine adjustment of the transparency and impact resistance of the graft copolymer to be produced. In case of using the alkyl (meth)acrylate for this purpose, it is used usually in an amount of not less than about 0.5 parts by weight per 100 parts by weight of the total of the butadiene polymer and the graft component. When the amount exceeds 3 parts by weight, the produced graft copolymer is in a better powder state, but the impact resistance imparting ability is decreased.

Representative examples of the crosslinking monomer are, for instance, divinyl benzen, monoethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and other known divinyl, diacrylate and dimethacrylate compounds, but are not limited thereto.

The alkyl (meth)acrylates used with the crosslinking monomer are preferably those having a C₁ to C₈ alkyl group. Representative examples thereof are, for instance, butyl acrylate and methyl methacrylate. They may be used alone or in admixture thereof.

The reaction condition for the treatment of the butadiene polymer prior to the graft polymerization is not particularly limited. In case that the butadiene polymer has been prepared by emulsion polymerization, it is convenient to add the crosslinking monomer and the alkyl (meth)acrylate to the obtained reaction mixture and then to conduct the reaction under the same conditions as the emulsion polymerization, for example, at a temperature of 50° to 70° C for 0.5 to 2 hours.

In the graft polymerization step, 15 to 35 parts by weight, preferably 20 to 30 parts by weight, of the monomer mixture (a) consisting of 50 to 95 % by weight, preferably 70 to 90 % by weight, of an aromatic vinyl monomer, 0.1 to 40 % by weight, preferably 10 to 30 % by weight, of a vinyl cyanide and 0 to 40 % by weight, preferably 0 or 0.1 to 20 % by weight, of other vinyl monomer copolymerizable with them is emulsion-polymerized in the presence of 85 to 65 parts by weight, preferably 80 to 70 parts by weight, of the butadiene polymer (b). For obtaining a satisfactory ability in imparting the impact resistance to vinyl chloride resins, it is necessary that the produced graft copolymer has a butadiene content of at least 60 % by weight, preferably at least 63% by weight. Also, when the amount of the graft component (a) is less than 15 by weight, the graft copolymer is apt to become a massive material and no good powder is obtained, and when it is more than 35 parts by weight, the impact resistance is decreased.

The aromatic vinyl monomer serves to prevent lowering of the refractive index of the produced graft copolymer (reinforcing agent) owing to the high butadiene content, thereby bringing the refractive index of the reinforcing agent close to that of vinyl chloride resins. Also, the vinyl cyanide monomer is used in order to prevent lowering of the physical properties such as transparency, impact resistance and powder characteristics resulting from the use of aromatic vinyl monomer included in a high proportion in the grafting portion. When the content of the aromatic vinyl monomer in the graft component (a) is less than 50 % by weight, the refractive index of the reinforcing agent becomes too small, and when it is more than 95% by weight, the physical properties such as transparency, impact resistance and powder characteristics are lowered. The vinyl cyanide monomer should be used in an amount of at least 0.1 % by weight for obtaining substantial effects produced by its use. When the amount of the vinyl cyanide monomer is over 40 % by weight, the physical properties such as transparency and impact resistance are lowered.

The other vinyl monomers copolymerizable with aromatic vinyl monomer and vinyl cyanide monomer may be optionally used when it is desired to improve the processability. If the other vinyl monomers are used in an amount over 40 % by weight, it becomes difficult to bring the refractive index of the reinforcing agent close to that of vinyl chloride resins.

Representative aromatic vinyl monomer used in the graft polymerization is styrene, and representative vinyl cyanide is acrylonitrile. Examples of the copolymerizable other vinyl monomers used in the graft polymerization are, for instance, alkyl acrylates and alkyl methacrylates, preferably those having a C₁ to C₅ alkyl group, such as butyl acrylate and methyl methacrylate, acrylic acid and methacrylic acid, but are not limited thereto. These monomers may be used alone or in admixture thereof.

The method of graft polymerization is not limited to a specific method. For example, the polymerization may be carried out in a normal polymerization manner wherein monomers are added to an aqueous latex of the butadiene polymer and are emulsion polymerized, in a manner wherein after agglomerating the butadiene polymer particles to form larger particles by adding an acid to the aqueous latex, the graft polymerization is conducted, or in a manner wherein a water-soluble electrolyte is added to the aqueous latex prior to the graft polymerization, thereby agglomerating the latex particles to form larger particles during the graft polymerization.

In the graft polymerization, the monomers may be added to the polymerization system at once, intermittently, continuously, or in stages wherein the monomer composition in each stage may be the same or different from each other.

From the viewpoint of the transparency of molded end products made from the resin composition of the invention, it is preferable that the graft copolymer in the latex obtained by the graft polymerization have a weight average particle size of 500 to 2,500 angstroms, which can be measured by an electron microscope, so that the refractive index of the graft copolymer used as the reinforcing agent for vinyl chloride resins comes close to that of the vinyl chloride resins. Typically, it is preferable that the difference in refractive index between the reinforcing agent and the vinyl chloride resins is from about 0 to about 0.01.

From the obtained latex of the graft copolymer, a polymer powder is obtained by adding an acid and/or a salt to the latex to coagulate the polymer particles, thermally treating, washing the polymer particles with water, dehydrating and drying. The powder is blended as a reinforcing agent with a vinyl chloride resin in an amount of 3 to 30 % by weight based on the total weight of the powder and the vinyl chloride resin in a usual manner to give the resin composition of the present invention. When the amount of the graft copolymer is less than 3 % by weight, no satisfactory improvement of the impact resistance is obtained. When it is more than 30 % by weight, both the transparency and the impact resistance of the vinyl chloride resins are decreased.

The reinforcing agent according to the present invention is applicable to any of those generally called vinyl chloride resins or polymers, polyvinyl chloride resins or the like, e.g. vinyl chloride homopolymer, vinyl chloride copolymers having a vinyl chloride content of at least about 80 % by weight, and post-chlorinated polyvinyl chloride.

The composition of the present invention may contain usual additives used for vinyl chloride resins, such as stabilizer, lubricant, and the like.

The resin composition of the present invention can be formed into molded articles, for example, by injection molding, calendering, blow molding, and the like. The molded articles have a high impact resistance and a good transparency and are suitably used for the purposes such as bottles and sheets.

The present invention is more specifically described and explained by means of the following Examples, in which all parts and % are by weight unless otherwise noted. It is to be understood that the present invention as claimed is not limited to these Examples.

Example 1

A polymerization vessel equipped with a stirrer was charged with 200 parts of water, 1.5 parts of sodium oleate, 0.002 part of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 part of disodium ethylenediaminetetraacetate, 0.2 part of formaldehyde sodium sulfoxylate, 0.2 part of tripotassium phosphate, 88 parts of butadiene, 12 parts of styrene, 1.0 part of divinyl benzene and 0.1 part of diisopropylbenzene hydroperoxide. The polymerization was carried out at 50°C for 15 hours to give a rubber latex of which the weight average particle size of polymer particles was 800 angstroms (hereinafter referred to as "rubber latex A"). The polymerization conversion was 99 %.

To 225 parts of the rubber latex A (solid matter: 75 parts) were added 60 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the latex was then continuously added a mixture of 21 parts of styrene, 1.0 part of methyl methacrylate, 3.0 parts of acrylonitrile and 0.1 part of cumene hydroperoxide at 70°C over 4 hours, and the polymerization was further continued for 1 hour to give an aqueous latex of a graft copolymer.

Sulfuric acid was added to the obtained graft polymer latex to deposit the polymer, and the polymer powder through heat treating, rinsing, dehydrating and drying.

To 91 parts of polyvinyl chloride (average degree of polymerization: 700) containing 1.2 parts of octyl tin mercaptide stabilizer, 0.8 part of glycerol ricinoleate and 0.2 part of a montanic acid ester was added 9 parts of the graft copolymer powder as a reinforcing agent. The mixture was kneaded for 8 minutes by rolls of 170°C, and was pressed for 15 minutes by heat pressure rolls of 190°C to give Izod impact test specimens having a thickness of 6 mm and transparent sheets having a thickness of 5 mm. The Izod impact strength was measured according to JIS K 7110, and the light transmission was measured according to JIS K 6714. The results are shown in Table 1.

Example 2

A polymerization vessel equipped with a stirrer was charged with 200 parts of water, 1.5 parts of sodium oleate, 0.002 part of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 parts of disodium ethylenediaminetetraacetate, 0.2 part of formaldehyde sodium sulfoxylate, 0.2 part of tripotassium phosphate, 68 parts of butadiene, 12 parts of styrene, 1.0 part of divinyl benzene and 0.1 part of diisopropylbenzene hydroperoxide. The polymerization was carried out at 50°C for 10 hours. After confirming that the polymerization conversion was over 95 %, 20 parts of butadiene and 0.05 part of diisopropylbenzene hydroperoxide were added to the system, and the polymerization was further continued for 7 hours to give a latex B of rubber particles having a weight average particle size of 800 angstroms. The polymerization conversion was 99 %.

A graft copolymer (reinforcing agent) was prepared in the same manner as in Example 1 except that 225 parts of the thus obtained rubber latex B was used in the graft polymerization. A vinyl chloride resin composition was prepared in the same manner and estimated. The results are shown in Table 1.

Example 3

The rubber latex B was prepared in the same manner as in Example 2.

A polymerization vessel was charged with 225 parts of the rubber latex B, 60 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the vessel was continuously added a mixture of 9 parts of styrene, 3 parts of acrylonitrile and 0.05 part of cumene hydroperoxide at 70°C over 2 hours. After further continuing the polymerization for 30 minutes, 12 parts of styrene, 1.0 part of methyl methacrylate and 0.05 part of cumene hydroperoxide were continuously added over 2 hours. The polymerization was further continued for 1 hour and finished to give an aqueous latex of a graft copolymer. The graft copolymer powder was obtained from the latex and blended with polyvinyl chloride to give a resin composition in the same manner as in Example 1. The results are shown in Table 1.

Example 4

A polymerization vessel equipped with a stirrer was charged with 200 parts of water, 1.5 parts of sodium oleate, 0.002 part of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 part of disodium ethylenediaminetetraacetate, 0.2 part of formaldehyde sodium sulfoxylate, 0.2 part of tripotassium phosphate, 74 parts of butadiene, 6 parts of styrene, 1.0 part of divinyl benzene and 0.1 part of diisopropylbenzene hydroperoxide. The polymerization was carried out at 50°C for 10 hours. After confirming that the polymerization conversion was not less than 95 %, 20 parts of butadiene and 0.05 part of diisopropylbenzene hydroperoxide were added to the system, and the polymerization was further continued for 7 hours to give a latex C of a butadiene copolymer having a weight average particle size of 800 angstroms. The polymerization conversion was 99 %.

To 210 parts of the rubber latex C (solid matter: 70 parts) were added 70 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the latex was then continuously added a mixture of 24 parts of styrene, 6.0 parts of acrylonitrile and 0.1 part of cumene hydroperoxide at 70°C over 4 hours, and the polymerization was further continued for 1 hour to give an aqueous latex of a graft copolymer.

From the thus obtained latex, the graft copolymer powder was obtained and incorporated into polyvinyl chloride in the same manner as in Example 1. The results are shown in Table 1.

Example 5

The rubber latex A was prepared in the same manner as in Example 1.

To 225 parts of the rubber latex A (solid matter: 75 parts) were added 60 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride.

To the resulting mixture were added 1.0 part of divinyl benzene, 1.0 part of butyl acrylate and 0.1 part of cumene hydroperoxide, and the reaction was carried out at 70 °C for 1 hour.

Then, in order to conduct the graft polymerization, a mixture of 21 parts of styrene, 1.0 part of methyl methacrylate, 3.0 parts of acrylonitrile and 0.1 part of cumene hydroperoxide was continuously added to the reaction mixture at 70 °C over 4 hours. The polymerization was further continued for 1 hour to give an aqueous latex of a graft copolymer.

A resin composition was prepared and estimated in the same manner as in Example 1. The results are shown in Table 1.

Example 6

The procedure of Example 2 was repeated except that before adding the monomer mixture to the rubber latex B for the graft polymerization, 1.0 part of divinyl benzene, 1.0 part of butyl acrylate and 0.1 part of cumene hydroperoxide were added and reacted at 70 °C for 1 hour.

The results are shown in Table 1.

Example 7

The procedure of Example 3 was repeated except that before adding the monomer mixture to the rubber latex B for the graft polymerization, 1.0 part of divinyl benzene, 1.0 part of butyl acrylate and 0.1 part of cumene hydroperoxide were added and reacted at 70 °C for 1 hour.

The results are shown in Table 1.

Comparative Example 1

A polymerization vessel equipped with a stirrer was charged with 200 parts of water, 1.5 parts of sodium oleate, 0.002 part of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.005 part of disodium ethylenediaminetetraacetate, 0.2 part of formaldehyde sodium sulfoxylate, 0.2 part of tripotassium phosphate, 77 parts of butadiene, 23 parts of styrene, 1.0 part of divinyl benzene and 0.1 part of diisopropylbenzene hydroperoxide. The polymerization was carried out at 50 °C for 15 hours to give an aqueous latex D of a butadiene copolymer having a weight average particle size of 800 angstroms. The polymerization conversion was 99 %.

To 180 parts of the obtained rubber latex D (solid matter: 60 parts) were added 70 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the resulting mixture were continuously added 20 parts of styrene, 20 parts of methyl methacrylate and 0.1 part of cumene hydroperoxide at 70 °C over 5 hours. The polymerization was further continued for 1 hour to give an aqueous latex of a graft copolymer.

A resin composition was prepared and estimated in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 2

To 225 parts of the rubber latex D prepared in the same manner as in Comparative Example 1 (solid matter: 75 parts) were added 60 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the resulting mixture were continuously added 12.5 parts of styrene, 12.5 parts of methyl methacrylate and 0.1 part of cumene hydroperoxide at 70 °C over 4 hours. The polymerization was further continued for 1 hour to give an aqueous latex of a graft copolymer.

A resin composition was prepared and estimated in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 3

To 257 parts of the rubber latex D (solid matter: 85.7 parts) prepared in the same manner as in Comparative Example 1 were added 50 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 part of potassium chloride. To the resulting mixture was continuously added a mixture of 7.15 parts of styrene, 7.15 parts of methyl methacrylate and 0.1 part of cumene hydroperoxide at 70°C over 3 hours. The polymerization was further continued for 1 hour to give a latex of a graft copolymer.

A resin composition was prepared and estimated in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 4

To 225 parts of the rubber latex B (solid matter: 75 parts) prepared in the same manner as in Example 2 were added 60 parts of water, 0.002 part of ferrous sulfate, 0.004 part of disodium ethylenediaminetetraacetate, 0.1 part of formaldehyde sodium sulfoxylate and 1.5 parts of potassium chloride. To the resulting mixture was continuously added a mixture of 12.5 parts of styrene, 12.5 parts of methyl methacrylate and 0.1 part of cumene hydroperoxide at 70°C over 4 hours. The polymerization was further continued for 1 hour to give a latex of a graft copolymer.

A resin composition was prepared and estimated in the same manner as in Example 1. The results are shown in Table 1.

Comparative Example 5

The procedure of Comparative Example 4 was repeated except that a monomer mixture of 21 parts of styrene, 4 parts of methyl methacrylate and 0.1 part of cumene hydroperoxide was used in the graft polymerization.

The results are shown in Table 1.

Table 1

Reinforcing agent						Properties of molded PVC composition			
Rubber latex (solid: parts)	Treatment of rubber (parts)	Graft component (parts)			Refractive index (N _D)	State of powder	Izod impact strength		Light trans- mission(%)
		1st stage	2nd stage	Bu con- tent (%)			23°C	0°C	
Ex. 1 A (75)	-	ST (21) MMA (1) AN (3)	-	66	○	1.5389	58	12.2	71
Ex. 2 B (75)	-	ST (21) MMA (1) AN (3)	-	66	○	1.5389	57	12.0	75
Ex. 3 B (75)	-	ST (9) AN (3)	ST (12) MMA (1)	66	○	1.5389	58	12.1	76
Ex. 4 C (70)	-	ST (24) AN (6)	-	65.8	○	1.5379	50	13.9	69
Ex. 5 A (75)	DVB (1) BA (1)	ST (21) MMA (1) AN (3)	-	66	⊙	1.5389	62	11.7	73
Ex. 6 B (75)	DVB (1) BA (1)	ST (21) MMA (1) AN (3)	-	66	⊙	1.5389	60	11.2	76

- continued -

- continued -

Reinforcing agent										Properties of molded PVC composition		
Rubber latex (solid: parts)		Treatment of rubber (parts)	Graft component (parts)				Izod impact strength	Light trans- mission(%)				
			1st stage	2nd stage	Bu con- tent (%)	State of powder				Refractive index (N _D)		
Ex. 7	B (75)	DVB (1) BA (1)	ST (9) AN (3)	ST (12) MMA(1)	66	⊙	1.5389	61	11.6	77		
Com. Ex. 1	D (60)	-	ST (20) MMA (20)	-	46	⊙	1.5380	22	4.0	77		
Com. Ex. 2	D (75)	-	ST (12.5) MMA (12.5)	-	58	X	1.5360	40	6.1	72		
Com. Ex. 3	D (85.7)	-	ST (7.15) MMA (7.15)	-	66	XX	1.5350	25	6.2	65		
Com. Ex. 4	B (75)	-	ST (12.5) MMA (12.5)	-	66	X	1.5296	59	12.0	51		
Com. Ex. 5	B (75)	-	ST (21) MMA (4)	-	66	X	1.5382	30	4.0	66		

(Notes) Bu: Butadiene

ST: Styrene

MMA: Methyl methacrylate

DVB: Divinyl benzene

BA: Butyl acrylate

State of powder: ⊙: Very good

○: Good

X : Bad

XX: Very bad

In addition to the ingredients used in the Examples, other ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL

1. A vinyl chloride resin composition which comprises:

(A) 3 to 30 parts by weight of a graft copolymer having a butadiene content of at least 60 % by weight prepared by reacting (i) 0.1 to 3 parts by weight of a crosslinking monomer and (ii) 0 to 3 parts by weight of at least one of alkyl acrylates and alkyl methacrylates in the presence of (b) 85 to 65 parts by weight of a butadiene polymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of other vinyl monomers copolymerizable therewith, and then subjecting the reaction product to emulsion polymerization with (a) 15 to 35 parts by weight of a monomer mixture of 50 to 95 % by weight of an aromatic vinyl monomer, 0.1 to 40 % by weight of a vinyl cyanide monomer and 0 to 40 % by weight of other vinyl monomers copolymerizable therewith, the total of said butadiene polymer (b) and said monomer mixture (a) being 100 parts by weight and the amounts of the components (i) and (ii) being based on 100 parts by weight of the total of the components (a) and (b), and

(B) 97 to 70 parts by weight of a vinyl chloride resin.

2. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of at least one other vinyl monomer copolymerizable with butadiene selected from the group consisting of an aromatic vinyl compound, an alkyl acrylate having a C₁ to C₅ alkyl group and a crosslinking monomer.

3. The composition of claim 1 or 2, wherein said graft copolymer has a butadiene content of at least 63 % by weight.

4. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene and styrene.

5. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene, styrene and a crosslinking monomer.

6. The composition of any of claims 1 to 5, wherein said aromatic vinyl monomer in said monomer mixture (a) is styrene.

7. The composition of any of claims 1 to 6, wherein said vinyl cyanide monomer in said monomer mixture (a) is acrylonitrile.

8. The composition of any of claims 1 to 5, wherein said monomer mixture (a) contains 50 to 95 % by weight of styrene, 0.1 to 40 % by weight of acrylonitrile and 0.01 to 20 % by weight of other vinyl monomers copolymerizable therewith.

(Notes) Bu: Butadiene

ST: Styrene

MMA: Methyl methacrylate

DVB: Divinyl benzene

BA: Butyl acrylate

State of powder: ⊙: Very good

○: Good

X : Bad

XX: Very bad

In addition to the ingredients used in the Examples, other ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL

1. A vinyl chloride resin composition which comprises:

(A) 3 to 30 parts by weight of a graft copolymer having a butadiene content of at least 60 % by weight prepared by reacting (i) 0.1 to 3 parts by weight of a crosslinking monomer and (ii) 0 to 3 parts by weight of at least one of alkyl acrylates and alkyl methacrylates in the presence of (b) 85 to 65 parts by weight of a butadiene polymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of other vinyl monomers copolymerizable therewith, and then subjecting the reaction product to emulsion polymerization with (a) 15 to 35 parts by weight of a monomer mixture of 50 to 95 % by weight of an aromatic vinyl monomer, 0.1 to 40 % by weight of a vinyl cyanide monomer and 0 to 40 % by weight of other vinyl monomers copolymerizable therewith, the total of said butadiene polymer (b) and said monomer mixture (a) being 100 parts by weight and the amounts of the components (i) and (ii) being based on 100 parts by weight of the total of the components (a) and (b), and

(B) 97 to 70 parts by weight of a vinyl chloride resin.

2. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of at least one other vinyl monomer copolymerizable with butadiene selected from the group consisting of an aromatic vinyl compound, an alkyl acrylate having a C₁ to C₅ alkyl group and a crosslinking monomer.

3. The composition of claim 1 or 2, wherein said graft copolymer has a butadiene content of at least 63 % by weight.

4. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene and styrene.

5. The composition of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene, styrene and a crosslinking monomer.

6. The composition of any of claims 1 to 5, wherein said aromatic vinyl monomer in said monomer mixture (a) is styrene.

7. The composition of any of claims 1 to 6, wherein said vinyl cyanide monomer in said monomer mixture (a) is acrylonitrile.

8. The composition of any of claims 1 to 5, wherein said monomer mixture (a) contains 50 to 95 % by weight of styrene, 0.1 to 40 % by weight of acrylonitrile and 0.01 to 20 % by weight of other vinyl monomers copolymerizable therewith.



9. The composition of claim 8, wherein said other vinyl monomer in said monomer mixture (a) is at least one member selected from the group consisting of an alkyl acrylate having a C₁ to C₅ alkyl group, an alkyl methacrylate having a C₁ to C₅ alkyl group, acrylic acid and methacrylic acid.
10. The composition of claim 1, wherein said crosslinking monomer is a member selected from the group consisting of divinyl compounds, diacrylate compounds and dimethacrylate compounds.

Claims for the following Contracting State : ES

1. A process for preparing a vinyl chloride resin composition which comprises preparing a graft copolymer having a butadiene content of at least 60 % by weight by reacting (i) 0.1 to 3 parts by weight of a crosslinking monomer and (ii) 0 to 3 parts by weight of at least one of alkyl acrylates and alkyl methacrylates in the presence of (b) 85 to 65 parts by weight of a butadiene polymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of other vinyl monomers copolymerizable therewith, and then subjecting the reaction product to emulsion polymerization with (a) 15 to 35 parts by weight of a monomer mixture of 50 to 95 % by weight of an aromatic vinyl monomer, 0.1 to 40 % by weight of a vinyl cyanide monomer and 0 to 40 % by weight of other vinyl monomers copolymerizable therewith, the total of said butadiene polymer (b) and said monomer mixture (a) being 100 parts by weight and the amounts of the components (i) and (ii) being based on 100 parts by weight of the total of the components (a) and (b), and combining 3 to 30 parts by weight of said graft copolymer with 97 to 70 parts by weight of a vinyl chloride resin.
2. The process of claim 1, wherein said butadiene polymer (b) is a copolymer of 82 to 100 % by weight of butadiene and 18 to 0 % by weight of at least one other vinyl monomer copolymerizable with butadiene selected from the group consisting of an aromatic vinyl compound, an alkyl acrylate having a C₁ to C₅ alkyl group and a crosslinking monomer.
3. The process of claim 1 or 2, wherein said graft copolymer has a butadiene content of at least 63 % by weight.
4. The process of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene and styrene.
5. The process of claim 1, wherein said butadiene polymer (b) is a copolymer of butadiene, styrene and a crosslinking monomer.
6. The process of any of claims 1 to 5, wherein said aromatic vinyl monomer in said monomer mixture (a) is styrene.
7. The process of any of claims 1 to 6, wherein said vinyl cyanide monomer in said monomer mixture (a) is acrylonitrile.
8. The process of any of claims 1 to 5, wherein said monomer mixture (a) contains 50 to 95 % by weight of styrene, 0.1 to 40 % by weight of acrylonitrile and 0.01 to 20 % by weight of other vinyl monomers copolymerizable therewith.
9. The process of claim 8, wherein said other vinyl monomer in said monomer mixture (a) is at least one member selected from the group consisting of an alkyl acrylate having a C₁ to C₅ alkyl group, an alkyl methacrylate having a C₁ to C₅ alkyl group, acrylic acid and methacrylic acid.
10. The process of claim 1, wherein said crosslinking monomer is a member selected from the group consisting of divinyl compounds, diacrylate compounds and dimethacrylate compounds.



Patentansprüche**Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL****1. Vinylchloridharz-Zusammensetzung, die umfaßt:**

A) 3 bis 30 Gew.-Teile eines Ppropf-Copolymers mit einem Butadiengehalt von mindestens 60 Gew.-%, hergestellt durch Umsetzung von (i) 0,1 bis 3 Gew.-Teilen eines vernetzenden Monomers und (ii) 0 bis 3 Gew.-Teilen mindestens eines Vertreters aus der Gruppe der Alkylacrylate und Alkylmethacrylate in Gegenwart von (b) 85 bis 65 Gew.-Teilen eines Butadien-Polymers aus 82 bis 100 Gew.-% Butadien und 18 bis 0 Gew.-% anderen, damit copolymerisierbaren Vinylmonomeren, und anschließendes Emulsionspolymerisieren des Reaktionsprodukts mit (a) 15 bis 35 Gew.-Teilen einer Monomer-Mischung von 50 bis 95 Gew.-% eines aromatischen Vinyl-Monomers, 0,1 bis 40 Gew.-% eines Vinylcyanid-Monomers und 0 bis 40 Gew.-% anderen, damit copolymerisierbaren Vinyl-Monomeren, wobei die Gesamtmenge des genannten Butadien-Polymers (b) und der genannten Monomer-Mischung (a) 100 Gew.-Teile beträgt und die Mengen der Komponenten (i) und (ii) auf 100 Gew.-Teile der Gesamtmenge der Komponenten (a) und (b) bezogen sind, und

B) 97 bis 70 Gew.-Teile eines Vinylchloridharzes.

2. Zusammensetzung nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer aus 82 bis 100 Gew.-% Butadien und 18 bis 0 Gew.-% mindestens eines anderen, mit Butadien copolymerisierbaren Vinyl-Monomers, ausgewählt aus der Gruppe, die besteht aus einer aromatischen Vinylverbindung, einem Alkylacrylat mit einer C₁-C₅-Alkylgruppe und einem vernetzenden Monomer, ist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin das Ppropf-Copolymer einen Butadiengehalt von mindestens 63 Gew.-% hat.

4. Zusammensetzung nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer von Butadien und Styrol ist.

5. Zusammensetzung nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer von Butadien, Styrol und einem vernetzenden Monomer ist.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin das aromatische Vinylmonomer in der genannten Monomer-Mischung (a) Styrol ist.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, worin das Vinylcyanid-Monomer in der genannten Monomer-Mischung (a) Acrylnitril ist.

8. Zusammensetzung nach einem der Ansprüche 1 bis 5, worin die Monomer-Mischung (a) 50 bis 95 Gew.-% Styrol, 0,1 bis 40 Gew.-% Acrylnitril und 0,01 bis 20 Gew.-% andere, damit copolymerisierbare Vinyl-Monomere enthält.

9. Zusammensetzung nach Anspruch 8, worin das andere Vinyl-Monomer in der Monomer-Mischung (a) mindestens ein Vertreter ist, der ausgewählt wird aus der Gruppe, die besteht aus einem Alkylacrylat mit einer C₁-C₅-Alkylgruppe, einem Alkylmethacrylat mit einer C₁-C₅-Alkylgruppe, Acrylsäure und Methacrylsäure.

10. Zusammensetzung nach Anspruch 1, worin das vernetzende Monomere ein Vertreter ist, der ausgewählt wird aus der Gruppe, die besteht aus Divinyl-Verbindungen, Diacrylat-Verbindungen und Dime-thacrylat-Verbindungen.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung einer Vinylchloridharz-Zusammensetzung, das umfaßt die Herstellung eines Ppropf-Copolymers mit einem Butadien-Gehalt von mindestens 60 Gew.-% durch Umsetzung von (i) 0,1 bis 3 Gew.-Teilen eines vernetzenden Monomers und (ii) 0 bis 3 Gew.-Teilen mindestens eines Vertreters aus der Gruppe der Alkylacrylate und Alkylmethacrylate in Gegenwart von (b) 85 bis 65 Gew.-Teilen eines Butadien-Polymers aus 82 bis 100 Gew.-% Butadien und 18 bis 0 Gew.-% anderen, damit copolymerisierbaren Vinylmonomeren, und anschließendes Emulsionspolymerisieren des Reak-



tionsprodukts mit (a) 15 bis 35 Gew.-Teilen einer Monomer-Mischung von 50 bis 95 Gew.-% eines aromatischen Vinyl-Monomers, 0,1 bis 40 Gew.-% eines Vinylcyanid-Monomers und 0 bis 40 Gew.-% anderen damit copolymerisierbaren Vinyl-Monomeren, wobei die Gesamtmenge von Butadien-Polymer (b) und Monomer-Mischung (a) 100 Gew.-Teile beträgt und die Mengen der Komponenten (i) und (ii) bezogen sind auf 100 Gew.-Teile der Gesamtmenge der Komponenten (a) und (b), und das Kombinieren von 3 bis 30 Gew.-Teilen des Pfropf-Copolymers mit 97 bis 70 Gew.-Teilen eines Vinylchloridharzes.

2. Verfahren nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer aus 82 bis 100 Gew.-% Butadien und 18 bis 0 Gew.-% mindestens eines anderen, mit Butadien copolymerisierbaren Vinyl-Monomers, ausgewählt aus der Gruppe, die besteht aus einer aromatischen Vinylverbindung, einem Alkylacrylat mit einer C₁-C₅-Alkylgruppe und einem vernetzenden Monomer, ist.
3. Verfahren nach Anspruch 1 oder 2, worin das Pfropf-Copolymer einen Butadiengehalt von mindestens 63 Gew.-% hat.
4. Verfahren nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer von Butadien und Styrol ist.
5. Verfahren nach Anspruch 1, worin das Butadien-Polymer (b) ein Copolymer von Butadien, Styrol und einem vernetzenden Monomer ist.
6. Verfahren nach einem der Ansprüche 1 bis 5, worin das aromatische Vinylmonomer in der genannten Monomer-Mischung (a) Styrol ist.
7. Verfahren nach einem der Ansprüche 1 bis 6, worin das Vinylcyanid-Monomer in der genannten Monomer-Mischung (a) Acrylnitril ist.
8. Verfahren nach einem der Ansprüche 1 bis 5, worin die Monomer-Mischung (a) 50 bis 95 Gew.-% Styrol, 0,1 bis 40 Gew.-% Acrylnitril und 0,01 bis 20 Gew.-% andere, damit copolymerisierbare Vinyl-Monomere enthält.
9. Verfahren nach Anspruch 8, worin das andere Vinyl-Monomer in der Monomer-Mischung (a) mindestens ein Vertreter ist, der ausgewählt wird aus der Gruppe, die besteht aus einem Alkylacrylat mit einer C₁-C₅-Alkylgruppe, einem Alkylmethacrylat mit einer C₁-C₅-Alkylgruppe, Acrylsäure und Methacrylsäure.
10. Verfahren nach Anspruch 1, worin das vernetzende Monomere ein Vertreter ist, der ausgewählt wird aus der Gruppe, die besteht aus Divinyl-Verbindungen, Diacrylat-Verbindungen und Dimethacrylat-Verbindungen.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL

1. Composition de résine de chlorure de vinyle comprenant :

- (A) 3 à 30 parties en poids d'un copolymère greffé ayant une teneur en butadiène d'au moins 60% en poids, préparé par réaction de (i) 0,1 à 3 parties en poids d'un monomère de réticulation et (ii) 0 à 3 parties en poids d'au moins un des acrylates et méthacrylates d'alkyle en présence de (b) 85 à 65 parties en poids d'un polymère de butadiène, de 82 à 100% en poids de polybutadiène et 18 à 0% en poids d'autres monomères vinyliques copolymérisables avec celui-ci, et en faisant subir au produit de la réaction une polymérisation en émulsion avec (a) 15 à 35 parties en poids d'un mélange de monomères de 50 à 95% en poids d'un monomère vinylique aromatique, 0,1 à 40% en poids d'un monomère cyanure de vinyle et 0 à 40% en poids d'autres monomères vinyliques copolymérisables avec ceux-ci, le total dudit polymère du butadiène (b) et dudit mélange de monomères (a) étant de 100 parties en poids et la somme des composants (i) et (ii) étant rapportée à 100 parties en poids du total des composants (a) et (b), et
- (B) 97 à 70 parties en poids d'une résine de chlorure de vinyle.



2. Composition selon la revendication 1, caractérisée en ce que ledit polymère de butadiène (b) est un copolymère de 82 à 100% en poids de butadiène et 18 à 0% en poids d'au moins un autre monomère vinylique, copolymérisable avec le butadiène, sélectionné dans le groupe consistant en un composé vinylique aromatique, un acrylate d'alkyle ayant un groupe alkyle en C₁ à C₅ et un monomère de réticulation.
3. Composition selon les revendications 1 ou 2, caractérisée en ce que ledit copolymère greffé a une teneur en butadiène d'au moins 63% en poids.
4. Composition selon la revendication 1, caractérisée en ce que ledit polymère du butadiène (b) est un copolymère de butadiène et de styrène.
5. Composition selon la revendication 1, caractérisée en ce que ledit polymère du butadiène (b) est un copolymère de butadiène, de styrène et d'un monomère de réticulation.
6. Composition selon l'une des revendications 1 à 5, caractérisée en ce que ledit monomère vinylique aromatique dudit mélange de monomères (a) est le styrène.
7. Composition selon l'une des revendications 1 à 6, caractérisée en ce que ledit monomère cyanure de vinyle dudit mélange de monomères (a) est l'acrylonitrile.
8. Composition selon l'une des revendications 1 à 5, caractérisée en ce que ledit mélange de monomères (a) contient 50 à 95% en poids de styrène, 0,1 à 40% en poids d'acrylonitrile et 0,01 à 20% en poids d'autres monomères vinyliques copolymérisables avec ceux-ci.
9. Composition selon la revendication 8, caractérisée en ce que ledit autre monomère vinylique dudit mélange de monomères (a) est au moins un membre sélectionné dans le groupe consistant en un acrylate d'alkyle ayant un groupe alkyle en C₁ à C₅, un méthacrylate d'alkyle ayant un groupe alkyle en C₁ à C₅, l'acide acrylique et l'acide méthacrylique.
10. Composition selon la revendication 1, caractérisée en ce que ledit monomère de réticulation est un membre sélectionné dans le groupe consistant en des composés divinyliques, des composés diacrylates et des composés diméthacrylates.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'une composition de résine de chlorure de vinyle, comprenant la préparation d'un copolymère greffé, d'une teneur en butadiène d'au moins 60% en poids, par réaction de (i) 0,1 à 3 parties en poids d'un monomère de réticulation et de (ii) 0 à 3 parties en poids d'au moins un des acrylates et méthacrylates d'alkyle en présence de (b) 85 à 95 parties en poids d'un polymère de butadiène de 82 à 100% en poids de butadiène et 18 à 0% en poids d'autres monomères vinyliques copolymérisables avec celui-ci, et en soumettant le produit de la réaction à une polymérisation en émulsion avec (a) 15 à 35 parties en poids d'un mélange de monomères de 50 à 95 % en poids d'un monomère vinylique aromatique, 0,1 à 40% en poids d'un monomère cyanure de vinyle et 0 à 40% en poids d'autres monomères vinyliques copolymérisables avec ceux-ci, le total des quantités du polymère du butadiène (b) et dudit mélange de monomères (a) étant de 100 parties en poids et la somme des composants (i) et (ii) étant rapportée à 100 parties en poids du total des composants (a) et (b), et en combinant de 3 à 30 parties en poids dudit copolymère avec 97 à 70 parties en poids d'une résine de chlorure de vinyle.
2. Procédé selon la revendication 1, caractérisé en ce que ledit polymère de butadiène (b) est un copolymère de 82 à 100% en poids de butadiène et 18 à 0% en poids d'au moins un autre monomère vinylique copolymérisable avec le butadiène, sélectionné dans le groupe consistant en un composé vinylique aromatique, un acrylate d'alkyle ayant un groupe alkyle en C₁ à C₅ et un monomère de réticulation.
3. Procédé selon les revendications 1 ou 2, caractérisé en ce que ledit copolymère greffé a une teneur en butadiène d'au moins 63% en poids.



4. Procédé selon la revendication 1, caractérisé en ce que ledit polymère du butadiène (b) est un copolymère de butadiène et de styrène.
5. Procédé selon la revendication 1, caractérisé en ce que ledit polymère du butadiène (b) est un copolymère de butadiène, de styrène et d'un monomère de réticulation.
6. Procédé selon l'une des revendications 1 à 5, caractérisé en ce que ledit monomère vinylique aromatique dudit mélange de monomères (a) est le styrène.
7. Procédé selon l'une des revendications 1 à 6, caractérisé en ce que ledit monomère cyanure de vinyle dudit mélange de monomères (a) est l'acrylonitrile.
8. Procédé selon l'une des revendications 1 à 5, caractérisé en ce que ledit mélange de monomères (a) contient 50 à 95% en poids de styrène, 0,1 à 40% en poids d'acrylonitrile et 0,01 à 20% en poids d'autres monomères vinyliques copolymérisables avec ceux-ci.
9. Procédé selon la revendication 8, caractérisé en ce que ledit autre monomère vinylique dudit mélange de monomères (a) est au moins un membre sélectionné dans le groupe consistant en un acrylate d'alkyle ayant un groupe alkyle en C₁ à C₅, un méthacrylate d'alkyle ayant un groupe alkyle en C₁ à C₅, l'acide acrylique et l'acide méthacrylique.
10. Procédé selon la revendication 1, caractérisé en ce que ledit monomère de réticulation est un membre sélectionné parmi le groupe consistant en des composés divinyliques, des composés diacrylates et des composés diméthacrylates.

