Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
Description

TECHNICAL FIELD

[0001] The present invention relates to a resin composition for a primer that has excellent adhesion to substrates of polypropylene and like polyolefin resins and to melamine and various like coatings and has excellent low-temperature storage stability.

BACKGROUND OF THE INVENTION

[0002] Offering many advantages such as high productivity, high design flexibility, light weight, rustproofing, high impact resistance, etc., plastics are used these days in a wide variety of applications for automotive parts, electronic parts, building materials and the like. In particular, since polyolefin resins are inexpensive and have excellent moldability, chemical resistance, water resistance, impact resistance, and electrical properties, they have been widely used as industrial materials and are one of the types of material for which demand is expected to further increase in the future.

[0003] However, unlike acrylic resins and similar synthetic polar resins, polyolefin resins have drawbacks due to their crystallinity and nonpolarity, i.e., it is difficult to coat or bond them. Primers containing weakly chlorinated polyolefins that are chlorinated to 10-40 wt.% as a binder have heretofore been used to coat or bond such low-adhesion polyolefin resins.

[0004] When the cost of transportation or the amount of solvent used is considered, primers should preferably have a large solids content. However, an excessive solids content results in decreased flowability or increased viscosity at low temperatures, adversely affecting primers in practical applications, for example, impaired solubility in coatings and workability during spray coating. Moreover, the storage stability at low temperatures is also adversely affected. To control viscosity, if the molecular weight of the resins is lowered by degradation or like methods, or low-molecular-weight rosin ester resins are added, the initial adhesion and gasohol resistance are significantly impaired.

[0005] Recently, the coating technique typically employed to reduce coating lines or costs is wet-on-wet coating in which primers and coatings are applied sequentially and baked only once. However, with such coating methods, it has been impossible to obtain sufficient adhesion particularly when melamine coatings are used. This is presumably because intermediate layers are created between primers and melamine coatings due to the high polarity of melamine resins and the low polarity of conventional primers. Therefore, resin compositions for high polarity primers are required.

DISCLOSURE OF THE INVENTION

[0006] An object of the present invention is to provide a resin composition for a primer that has excellent adhesion to polyolefin resin substrates and melamine coatings and has enhanced low-temperature storage stability and gasohol resistance.

[0007] Other objects and characteristics of the present invention will become evident by the disclosure provided hereinbelow.

[0008] The inventors conducted extensive research and found that the combination of a specific chlorinated polyolefin and a specific hydroxyl-containing petroleum resin can attain the objects described above. The inventors thereby accomplished the present invention.

[0009] In particular, the present invention provides the resin compositions for primers described below:

Item 1. A resin composition for a primer comprising (a) 100 parts by weight of a chlorinated polyolefin having a chlorine content of 5-50 wt.% and a weight-average molecular weight of 30000-120000, and (b) 15-80 parts by weight of at least one hydroxyl-containing petroleum resin, wherein the hydroxyl-containing petroleum resin has a hydroxyl value of 10-250 mgKOH/g, a softening point of 60-200°C and a weight-average molecular weight of 200-3000.

Item 2. The resin composition for a primer according to Item 1 further comprising (c) an organic solvent.

Item 3. The resin composition for a primer according to Item 1 or 2, wherein the chlorinated polyolefin is an acid-modified chlorinated polyolefin produced by graft-copolymerization with 1-10 wt.% of at least one member selected from the group consisting of α,β-unsaturated carboxylic acids and their acid anhydrides.

Item 4. The resin composition for a primer according to any one of Items 1-3, wherein the hydroxyl-containing petroleum resin is hydrogenated.

Item 5. The resin composition for a primer according to any one of Items 2-4, wherein the organic solvent is at least one member selected from the group consisting of aromatic hydrocarbons, alicyclic hydrocarbons, esters and ketones.
Chlorinated polyolefins usable herein may be produced by chlorinating polyolefins. Examples thereof include those that are further acid-modified and contain carboxylic group(s). Such chlorinated polyolefins can be readily produced according to known methods. For example, acid-modified chlorinated polyolefins can be obtained by graft-copolymerizing starting polyolefins with at least one member selected from the group consisting of \( \alpha, \beta \)-unsaturated carboxylic acids and their acid anhydrides, and then injecting chlorine gas in the presence of a solvent. They can also be obtained by chlorinating starting polyolefins and then graft-copolymerizing the chlorinated polyolefins with at least one member selected from the group consisting of \( \alpha, \beta \)-unsaturated carboxylic acids and their acid anhydrides.

Examples of starting polyolefins are propylene-based polyolefins including crystalline polypropylene, noncrystalline polypropylene and propylene-ethylene copolymers. Such polymers can be used alone or in combination. Among these, preferable are crystalline polypropylenes such as isotactic polypropylene and syndiotactic polypropylene, with isotactic polypropylene being particularly preferable.

The olefin portion of the hydroxyl-containing petroleum resins may be stabilized as necessary by hydrogenation, nol-modified dicyclopentadiene resins, and phenol-modified C9 petroleum resins.

Examples of polymerizable monomers contained in petroleum fractions are isoprene, \( \alpha \)-methylstyrene, indene, methyl \( \beta \)-pentene, methylbutene, pentadiene, cyclopentene and like monomers of the C5 fraction; styrene, vinyltoluene, \( \alpha \)-methylstyrene, indene, methyl indene and like monomers of the C9 fraction; cyclopentadiene, methylcyclopentadiene, ethylcyclopentadiene and like monomers of the cyclopentadiene portion including the dimers, trimers and codimers thereof; etc. Among these, preferable are crystalline polypropylenes such as isotactic polypropylene and syndiotactic polypropylene, with isotactic polypropylene being particularly preferable.

To obtain chlorinated polyolefins by chlorination, starting polyolefins or acid-modified polyolefins are dispersed or dissolved in a chlorinated solvent such as chloroform, carbon tetrachloride, tetrachloroethylene or the like, and reacted in the presence of a catalyst by injecting chlorine gas under ambient or increased pressure at 80-120°C.

The chlorine content of the chlorinated polyolefins (including the acid-modified chlorinated polyolefins) is 5-50 wt.%, preferably 10-40 wt. %.

The weight-average molecular weight of the chlorinated polyolefins (including the acid-modified chlorinated polyolefins) is 30000-120000, preferably 40000-80000.

Hydroxyl-containing petroleum resins usable herein refer to petroleum resins containing hydroxyl group(s) in their molecular structure due to some chemical bonding. Methods for producing such hydroxyl-containing petroleum resins are not limited. In view of industrial convenience, such petroleum resins are usually those that can be obtained by reacting polymerizable monomers contained in petroleum fractions with hydroxyl-containing compounds.

Examples of polymerizable monomers contained in petroleum fractions are \( \alpha \)-methylstyrene, \( \alpha \)-methylstyrene, indene, methyl indene and like monomers of the C9 fraction; cyclopentadiene, methylcyclopentadiene, ethylcyclopentadiene and like monomers of the cyclopentadiene portion including the dimers, trimers and codimers thereof; etc.

Examples of polymerizable monomers contained in petroleum fractions are isoprene, \( \alpha \)-pentene, \( \alpha \)-methylbutene, pentadiene, cyclopentene and like monomers of the C5 fraction; styrene, vinyltoluene, \( \alpha \)-methylstyrene, indene, methyl indene and like monomers of the C9 fraction; cyclopentadiene, methylcyclopentadiene, ethylcyclopentadiene and like monomers of the cyclopentadiene portion including the dimers, trimers and codimers thereof; etc.

Hydroxyl-containing compounds refer to phenolic compounds and hydroxyl-containing olefins. Examples thereof include phenols; cresol, xylol, \( \alpha \)-tert-butylphenol, \( \alpha \)-cytlylphenol, nonylphenol, vinylphenol and like alkyl-substituted phenols; allyl alcohol, crotyl alcohol, 1,4-butenediol, hydroxyethyl acrylate, hydroxyethyl methacrylate; 3-methyl-2-propene-1-ol, 2-methyl-3-propene-1-ol and like alkyl-substituted allyl alcohols; etc.

Methods for producing the hydroxyl-containing petroleum resins are not limited, and known methods can be employed. Examples include a method wherein a polymerizable monomer and a hydroxyl-containing compound are polymerized in the presence of a Friedel-Crafts catalyst; a method wherein a polymerizable monomer and a hydroxyl-containing compound are polymerized in the presence of a radical polymerization initiator; a method wherein a polymerizable monomer and a hydroxyl-containing compound are thermally polymerized in an autoclave; and like methods.

The hydroxyl-containing petroleum resins are selected from the group consisting of alcohol-modified dicyclopentadiene resins, alcohol-modified C9-dicyclopentadiene resins, phenol-modified C9-dicyclopentadiene resins, phenol-modified dicyclopentadiene resins, and phenol-modified C9 petroleum resins.

The olefin portion of the hydroxyl-containing petroleum resins may be stabilized as necessary by hydrogenation, hydration, oxidation, hydroboration, hydrohalogenation, halogenation, etc. Among these methods, hydrogenation is preferable since it is industrially convenient and can improve the color, odor and stability of the resin. Hydrogenation can be carried out according to conventional methods.

Although the extent of hydrogenation of the aromatic portion or olefinic portion of the hydroxyl-containing hydrogenated petroleum resins is not limited, it is preferable to completely hydrogenate the olefinic portion to improve color and stability.

Alternatively, the stability and color of the hydroxyl-containing petroleum resins may be improved by adding antioxidants, UV absorbers, reducing agents, etc.

The softening point of the hydroxyl-containing petroleum resins usable herein is preferably 60-200°C. Although
for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight as 100 parts by weight of starting oil. Using 0.6 wt.

Production Example 2 (Phenol-Modified C9 Petroleum Resin)

A cracked distillate fraction with a boiling range of 140-280°C generated during the steam-cracking of naphtha was used as 100 parts by weight of starting oil. Using 0.6 wt.% of boron trifluoride phenolate relative to the starting oil, polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to polymerization was carried out for 3 hours at 30°C in the presence of 3 parts by weight of phenol. Calcium hydroxide (3 parts by weight) was added to the polymerized oil thus obtained, and the mixture was stirred for 1 hour at 70°C to neutralize, and 3 parts by weight of activated clay was further added and the mixture was stirred for 30 more minutes. The polymerized oil obtained by filtering off the calcium hydroxide and activated clay was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin A having a softening point of 105°C, a color of 9
Gardner, a hydroxyl value of 72 mgKOH/g, and a weight-average molecular weight of 1350 (polystyrene equivalent obtained by gel permeation chromatography (GPC)).

Production Example 3 (Phenol-Modified Dicyclopentadiene Resin)

Dicyclopentadiene (100 parts by weight), 100 parts by weight of phenol and 80 parts by weight of xylene were introduced into an autoclave and reacted for 4 hours at 260°C in a nitrogen atmosphere, thereby giving a polymerized oil. This polymerized oil was distilled at 200°C at 2.7 kPa for 15 minutes to remove unreacted monomers, oligomers and the solvent, thereby giving Hydroxyl-Containing Petroleum Resin B having a softening point of 111°C, a color of 10 Gardner, a hydroxyl value of 157 mgKOH/g, and a weight-average molecular weight of 580 (polystyrene equivalent obtained by GPC).

Production Example 4 (Alcohol-Modified Dicyclopentadiene Resin)

Dicyclopentadiene (100 parts by weight), 100 parts by weight of allyl alcohol and 80 parts by weight of xylene were introduced into an autoclave and reacted for 2 hours at 270°C in a nitrogen atmosphere, thereby giving a polymerized oil. This polymerized oil was distilled to remove unreacted monomers, oligomers and the solvent at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin C having a softening point of 97.5°C, a color of 8 Gardner, a hydroxyl value of 210 mgKOH/g, and a weight-average molecular weight of 540 (polystyrene equivalent obtained by GPC).

Production Example 5 (Hydrogenated Alcohol-Modified Dicyclopentadiene Resin)

Hydroxyl-Containing Petroleum Resin C as obtained in Production Example 4 (100 parts by weight), 100 parts by weight of cyclohexane and 0.4 parts by weight of a stabilized nickel catalyst (manufactured by Nikki Chemical Co., Ltd., trade name: "N-113") were introduced into an autoclave and reacted for 5 hours at 270°C in a pressurized hydrogen atmosphere at 18 MPa. After filtering off the catalyst, the reaction mixture was distilled at 200°C at 2.7 kPa for 15 minutes, thereby giving Hydroxyl-Containing Petroleum Resin D having a softening point of 93°C, a color of 1 Gardner or less (200 Hazen), a hydroxyl value of 143 mgKOH/g, and a weight-average molecular weight of 530 (polystyrene equivalent obtained by GPC).

Production Example 6 (Hydrogenated Alcohol-Modified Dicyclopentadiene Resin)

Hydroxyl-Containing Petroleum Resin C as obtained in Production Example 4 (100 parts by weight), 100 parts by weight of cyclohexane and 2.0 parts by weight of a stabilized nickel catalyst (manufactured by Nikki Chemical Co., Ltd., trade name: "N-113") were introduced into an autoclave and reacted for 5 hours at 240°C in a pressurized hydrogen atmosphere at 18 MPa. After filtering off the catalyst, the reaction mixture was distilled at 220°C at 0.27 kPa for 30 minutes, thereby giving Hydroxyl-Containing Petroleum Resin E having a softening point of 118°C, a color of 1 Gardner or less (300 Hazen), a hydroxyl value of 190 mgKOH/g, and a weight-average molecular weight of 600 (polystyrene equivalent obtained by GPC).

Example 1

Chlorinated Polyolefin A was used as the chlorinated polyolefin and Hydroxyl-Containing Petroleum Resin A was used as the hydroxyl-containing petroleum resin. Twenty-wt.% toluene solutions were prepared for the chlorinated polyolefin and the hydroxyl-containing petroleum resin respectively. Both toluene solutions were mixed using the formulation (parts by weight) shown in Table 1 and sufficiently stirred, thereby giving a resin composition for a primer.

This resin composition for a primer was sprayed in an amount to attain a solid content of 6 g/m² onto a polypropylene substrate (manufactured by Mitsui Toatsu Chemicals, Inc.) degreased by isopropyl alcohol and left to stand for 10 minutes at room temperature to dry. A two-component urethane coating (manufactured by Kansai Paint Co., Ltd., "Retan PG80") was further spray-coated thereon in an amount of 60 g/m², and the substrate was dried for 30 minutes at 80°C. Similarly, a polypropylene substrate coated with the aforementioned resin composition for a primer was coated with a one-component melamine coating (manufactured by Kansai Paint Co., Ltd.) in the same manner as above, and the substrate was dried for 30 minutes at 120°C.

The low-temperature storage stability of the aforementioned resin composition for a primer and the properties of the coated films were evaluated according to the following methods. Table 2 shows the results.
[Low-Temperature Storage Stability]

[0045] The resin composition for a primer was left to stand at -5°C for up to 30 days. During that period, the number of days was counted until the resin composition started to gelate.

[Initial Adhesion (Bonding)]

[0046] Four days after drying, the coated surfaces of the test pieces were provided with a grid pattern of a hundred 1-mm squares by a cutter that reached through to the underlying polypropylene substrate. An adhesive cellophane tape was securely placed on the coated surfaces, and the tape was quickly peeled horizontal to the surface. This procedure was repeated 10 times. The test pieces were graded according to how many times the tape peeling was conducted before a square created on the coated surfaces was removed, i.e., if square(s) were removed the first time the tape peeling was conducted, this test piece was given 0 points, and if square(s) were removed the second time the tape peeling was conducted, this test piece was given 1 point. If a test piece exhibited no removal after ten rounds of tape peeling, this test piece was given 10 points, with 10 being full marks.

[Gasohol Resistance]

[0047] Seven days after drying, coated test pieces whose two ends had been cut off were immersed in a gasoline mixture (conventional unleaded gasoline : ethanol = 9 : 1 ). The time taken for the coating to peel to a distance of 3 mm from a cut edge of the coated test pieces was measured.

[Moisture Resistance]

[0048] Coated test pieces were immersed in 40°C warm water for 240 hours. The condition of the coated surface was visually observed and evaluated. The evaluation scale consists of A: excellent, B: good, and C: poor.

Examples 2-5

[0049] As shown in Table 1, resin compositions for a primer were prepared in the same manner as in Example 1 except that Hydroxyl-Containing Petroleum Resin A was replaced with Hydroxyl-Containing Petroleum Resin B, C, D or E. These resin compositions were evaluated and the results are shown in Table 2.

Example 6

[0050] As shown in Table 1, a resin composition for a primer was prepared in the same manner as in Example 4 except that the amount of the toluene solution of Hydroxyl-Containing Petroleum Resin D was altered to 25 parts by weight. This resin composition was evaluated and the results are shown in Table 2.

Example 7

[0051] As shown in Table 1, a resin composition for a primer was prepared in the same manner as in Example 4 except that the amount of the toluene solution of Hydroxyl-Containing Petroleum Resin D was altered to 66 parts by weight. This resin composition was evaluated and the results are shown in Table 2.

Comparative Example 1

[0052] A toluene solution of Chlorinated Polyolefin A, which does not contain a hydroxyl-containing petroleum resin, was used as a resin composition for a primer, and the properties thereof were evaluated. Table 2 shows the results.

Comparative Example 2

[0053] As shown in Table 1, a resin composition for a primer was prepared in the same manner as in Example 1 except that Hydroxyl-Containing Petroleum Resin A was replaced with a glycerol ester of rosin (weight-average molecular weight: 920, softening point: 100°C). This resin composition was evaluated and the results are shown in Table 2.
Comparative Example 3

[0054] As shown in Table 1, a resin composition for a primer was prepared in the same manner as in Example 1 except that Hydroxyl-Containing Petroleum Resin A was replaced with an unmodified C9 petroleum resin that contained no hydroxyl groups (weight-average molecular weight: 1100, softening point: 100°C). This resin composition was evaluated and the results are shown in Table 2.
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<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
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Table 1
As is clear from Table 2, compared with the resin composition for a primer of Comparative Example 1, the resin compositions for a primer of Examples 1-7 exhibit increased low-temperature storage stability and, with respect to the melamine coating, enhanced gasohol resistance. Furthermore, compared with the resin compositions for a primer of Comparative Examples 2 and 3, the resin compositions for a primer of Examples 1-7 exhibit increased adhesion and
gasohol resistance.

**Claims**

1. A resin composition for a primer comprising (a) 100 parts by weight of a chlorinated polyolefin having a chlorine content of 5-50 wt.% and a weight-average molecular weight of 30000-120000, and (b) 15-80 parts by weight of at least one hydroxyl-containing petroleum resin selected from the group consisting of alcohol-modified dicyclopentadiene resins, alcohol-modified C9-dicyclopentadiene resins, phenol-modified C9-dicyclopentadiene resins, phenol-modified C9 petroleum resins, wherein the hydroxyl-containing petroleum resin has a hydroxyl value of 10-250 mgKOH/g, a softening point of 60-200°C and a weight-average molecular weight of 200-3000.

2. The resin composition for a primer according to Claim 1 further comprising (c) an organic solvent.

3. The resin composition for a primer according to Claim 1 or 2, wherein the chlorinated polyolefin is an acid-modified chlorinated polyolefin produced by graft-copolymerization with 1-10 wt.% of at least one member selected from the group consisting of α,β-unsaturated carboxylic acids and their acid anhydrides.

4. The resin composition for a primer according to any one of Claims 1-3, wherein the hydroxyl-containing petroleum resin is hydrogenated.

5. The resin composition for a primer according to any one of Claims 2-4, wherein the organic solvent is at least one member selected from the group consisting of aromatic hydrocarbons, alicyclic hydrocarbons, esters and ketones.

**Revendications**

1. Composition de résines pour apprêt comprenant :

(a) 100 parties en poids d’une polyoléfine chlorée ayant une teneur en chlore de 5 à 50% en poids et un poids moléculaire moyen en poids de 30.000 à 120.000, et

(b) 15 à 80 parties en poids d’au moins une résine de pétrole contenant un groupe hydroxy choisie dans le groupe consistant en résines dicyclopentadiène modifiées par un alcool, résines en C9-dicyclopentadiène modifiées par un alcool, résines en C9-dicyclopentadiène modifiées par un phénol, résines dicyclopentadiène modifiées par un phénol et résines de pétrole en C9 modifiées par un phénol, dans laquelle la résine de pétrole contenant un groupe hydroxy a un indice hydroxy de 10 à 250 mg de KOH/g, un point de ramollissement de 60 à 200°C et un poids moléculaire moyen en poids de 200 à 3.000.

2. Composition de résines pour apprêt selon la revendication 1, comprenant de plus (c) un solvant organique.

3. Composition de résines pour apprêt selon la revendication 1 ou 2, dans laquelle la polyoléfine chlorée est une polyoléfine chlorée modifiée par un acide produced par copolymérisation greffée avec 1 à 10% en poids d’au moins un élément choisi dans le groupe consisant en acides carboxyliques α,β-insaturés et leurs anhydrides d’acide.

4. Composition de résines pour apprêt selon l’une quelconque des revendications 1 à 3, dans laquelle la résine de pétrole contenant un groupe hydroxy est hydrogénée.

5. Composition de résines pour apprêt selon l’une quelconque des revendications 2 à 4, dans laquelle le solvant organique est au moins un solvant choisi dans le groupe consistant en hydrocarbures aromatiques, hydrocarbures alicycliques, esters et cétones.

**Patentansprüche**

1. Harzzusammensetzung für ein Grundiermittel, welches (a) 100 Gewichtsteile eines chlorierten Polyolefins mit einem Chlorgehalt von 5 bis 50 Gewichtsprozent und einem gewichtsgemittelten Molekulargewicht von 30000 bis 120000 und (b) 15 bis 80 Gewichtsteile mindestens eines Hydroxyl-enthaltenden Erdölharzes, ausgewählt aus der Gruppe,
bestehend aus Alkohol-modifizierten Dicyclopentadienharzen, Alkohol-modifizierten C9-Dicyclopentadienharzen, Phenol-modifizierten C9-Dicyclopentadienharzen, Phenol-modifizierten Dicyclopentadienharzen und Phenol-modifizierten C9-Erdölharzen, wobei das Hydroxyl-enthaltende Erdölharz einen Hydroxylwert von 10 bis 250 mgKOH/g, einen Erweichungspunkt von 60 bis 200°C und ein gewichtsgemitteltes Molekulargewicht von 200 bis 300 aufweist, umfasst.

2. Harzzusammensetzung für ein Grundiermittel nach Anspruch 1, weiter umfassend (c) ein organisches Lösungsmittel.

3. Harzzusammensetzung für ein Grundiermittel nach Anspruch 1 oder 2, wobei das chiorierte Polyolefin ein Säure-modifiziertes chloriertes Polyolefin ist, welches durch Pfropfcopolymerisation mit 1 bis 10 Gewichtsprozent von mindestens einem Mitglied, ausgewählt aus der Gruppe, bestehend aus α, β-ungesättigten Carbonsäuren und deren Säureanhydriden, hergestellt ist.

4. Harzzusammensetzung für ein Grundiermittel nach einem der Ansprüche 1 bis 3, wobei das Hydroxyl-enthaltende Erdölharz hydriert ist.

5. Harzzusammensetzung für ein Grundiermittel nach einem der Ansprüche 2 bis 4, wobei das organische Lösungsmittel mindestens ein Mitglied, ausgewählt aus der Gruppe, bestehend aus aromatischen Kohlenwasserstoffen, alicyclischen Kohlenwasserstoffen, Estern und Ketonen ist.