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(54) Title: PRIMER COMPOSITION

(57) Abrégé/Abstract:

A primer composition containing a polyisocyanate component and a phosphate, preferably in an amount of 5 to 100 parts by weight, based on 100 parts by weight of the isocyanate component.



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PRIMER COMPOSITION

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ABSTRACT OF THE DISCLOSURE

10 A primer composition containing a polyisocyanate  
component and a phosphate, preferably in an amount of  
5 to 100 parts by weight, based on 100 parts by weight of  
the isocyanate component.

PRIMER COMPOSITION

## BACKGROUND OF THE INVENTION

## 5 1. Field of the Invention

The present invention relates to a primer composition capable of providing a satisfactory adhesion property to a nonadhesible or hard-to-bond material such as polyolefin and high solid paint (i.e., highly corrosion-resistant paint).

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## 2. Description of the Related Art

Recently, parts such as automobile parts heretobefore manufactured from steel materials are being substituted with resin products for the purpose of reducing the weight and cost thereof. Moreover, there has been increasing the proportion of a highly corrosion-resistant paint, namely, a so-called high solid paint, as paints for automobiles, etc.

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Those materials having excellent corrosion-resistant properties, such as resins (e.g., polyolefin) and high solid paints, generally have poor adhesion properties, and it is difficult to obtain the good adhesibility (or adhesion properties) when conventional primers are used.

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For this reason, attempts have been made to obtain good adhesibility when these hard-to-bond materials are bonded, by adding various additives to the primers. For example, Japanese Unexamined Patent Publication (Kokai) No. 61-152755 proposes a primer composition containing, for example, chlorinated polyolefin.

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However, these proposed primer compositions are still not sufficient to provide the desired good adhesive properties to the hard-to-bond materials, and therefore, there is a need for such a primer composition that can bond hard-to-bond materials with good adhesivity.

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## SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to solve the above-mentioned problems in the prior art and to provide a primer composition capable of providing a sufficient adhesivity even to hard-to-bond materials such as polyolefins and high solid paints.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a primer composition comprising a polyisocyanate component and a phosphate (or phosphoric acid salt).

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The primer composition of the present invention will now be illustrated in detail below.

The fundamental constitution of the primer composition according to the invention is the polyisocyanate component and the phosphate.

There are no particular limitations to the polyisocyanate component usable in the present invention. Examples of such a polyisocyanate component include 4,4'-diphenylmethane diisocyanate (MDI), tolylene diisocyanates (TDI), xylene diisocyanates (XDI), hexamethylene diisocyanate (HMDI), hydrogenated MDI, hydrogenated TDI, hydrogenated XDI, isophorone diisocyanate (IPDI), aromatic aliphatic polyisocyanate (e.g., arylalkyl polyisocyanates), aromatic polyisocyanates (e.g., aryl polyisocyanates), triphenylmethane triisocyanates, tris(p-isocyanatophenyl) thiophosphate, and mixtures thereof obtained by suitably mixing any above-mentioned compounds.

A combination of MDI, tris(p-isocyanatophenyl) thiophosphate and aromatic aliphatic isocyanate is preferably used.

The phosphate (or phosphoric acid salt) usable in the present invention is not specifically limited, and various phosphates can be used in the present invention. Typical examples of the phosphates suitably used in the

present invention are aluminum phosphate, zinc phosphate and aluminum dihydrogentripolyphosphate. Aluminum dihydrogentripolyphosphate is particularly preferably used in the present invention.

5           The above-mentioned phosphates may be subjected to various treatments.

          Especially, phosphates surface treated with Si and/or Zn, particularly, aluminum dihydrogentripolyphosphate surface treated with Si and/or Zn can provide  
10 extremely excellent adhesive properties, and more preferable results can be obtained therefrom. Furthermore, phosphates subjected to a dehydrating treatment are preferred in the present invention.

          In the primer composition of the present invention,  
15 there is no particular limitation as to the amount ratio of the phosphate to the polyisocyanate component. The ratio may be suitably determined according to the types of the polyisocyanate component and the phosphate. The phosphate is usually used in an amount of about 5 to  
20 100 parts by weight, more preferably 30 to 60 parts by weight, based on 100 parts by weight of the polyisocyanate component.

          When the phosphate is used in the amount as defined above, based on the polyisocyanate component, the effect  
25 of adding the phosphate can be sufficiently obtained, and the phosphate can be appropriately dispersed in the primer composition to provide the good adhesive properties.

          Furthermore, more preferable results for, for  
30 example, the percent cohesive failure of adhesive can be obtained by using the phosphate in an amount of 30 to 60 parts by weight, based on 100 parts by weight of the polyisocyanate component.

          The primer composition of the present invention may  
35 include, if necessary, various solvents, especially organic solvents.

          Any conventional solvents inactive to an isocyanate

group are usable in the present invention. Typical examples of the solvent usable in the present invention include ethyl acetate, methyl ethyl ketone (MEK), acetone and toluene.

5           The amount of the solvent added is appropriately determined according to, for example, the type of the polyisocyanate compound, and is not specifically restricted. Preferably, the amount is 500 to 1000 parts by weight, more preferably 600 to 800 parts by weight,  
10 based on 100 parts by weight of the polyisocyanate component.

          Furthermore, according to the present invention, various catalysts may be used in combination with the primer composition.

15           Examples of the catalyst usable in the present invention include amine catalysts such as triethylenediamine, pentamethylenediethylenetriamine, morpholine type amine and triethylamine, and tin catalysts such as di-n-octyltin dilaurate, dibutyltin  
20 dilaurate and stannous octoate.

          The amount of the catalyst added in the present invention is preferably determined according to, for example, the type of the polyisocyanate compound, and is not specifically limited. The amount is preferably about  
25 0.1 to 1 part by weight, more preferably 0.2 to 0.5 parts by weight, based on 100 parts by weight of the polyisocyanate component.

          In the primer composition of the present invention, there may be used, in combination, urethane resin such as  
30 polyester polyurethane resin and polyether polyurethane resin, polyester resin, and the like to obtain good working or processing properties. The amount of these resins added are not specifically restricted, but it is preferably 10 to 30 parts by weight, based on 100 parts  
35 by weight of the polyisocyanate component.

          Furthermore, a dehydrating agent inactive to isocyanate groups, such as synthetic zeolite may be used

in combination for securing the stability of the primer composition.

5 The primer composition of the present invention can be prepared by any various known methods for sufficiently mixing each of the components, for example, by mixing the components by a ball mill.

10 The primer composition according to the present invention may be used in the same manner as conventional isocyanate based primer compositions. The area or region to be bonded may be coated therewith by spraying, dried by allowing the area to stand for a suitable period of time, and bonded the area by a conventional method.

15 Examples of adhesives applicable to the primer composition of the present invention include urethane adhesives and epoxy adhesives.

20 Since the primer composition of the present invention as described above exhibits extremely good improvement in adhesive properties compared with conventional primer compositions, it can be extremely effectively utilized as a primer coating for effectively bonding between adhesive-resistant materials such as polyolefins (e.g., polyethylene and polypropylene), and high solid paints.

#### EXAMPLES

25 The present invention will now be further illustrated by, but is by no means limited to, the following Examples.

#### Examples 1 - 5 and Comparative Example 1

30 Various materials listed below were provided to prepare primer compositions.

Polyisocyanate component:

- a. MDI
- b. tris(p-isocyanatophenyl) thiophosphate (Desmodur HL, manufactured by Bayer Ltd.)
- 35 c. aromatic aliphatic isocyanate (Desmodur RFE, manufactured by Bayer Ltd.)

The mixture of the above-mentioned isocyanate

compounds with a molecular ratio of a:b:c being equal to 2:2:6

5 Solvent: ethyl acetate  
Desiccant: synthetic zeolite  
Catalyst: di-n-octyl dilaurate  
Urethane resin: Pandex T 5205 (manufactured by Dainippon Ink K.K.)

10 Phosphate a: aluminum dihydrogentripolyphosphate (K-WHITE #84S, treated with Si and Zn, manufactured by Teika Corporation)

Phosphate b: aluminum dihydrogentripolyphosphate ( $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ )

15 The above-mentioned materials were mixed in ratios (ratios by weight) listed in Table 1 below to give various primer compositions. The mixing was effected at room temperature for 48 hours by a ball mill.

20 Polypropylene containing 40% by weight of glass fibers and a high solid paint for automobiles (with which a steel sheet was coated) were bonded together, as samples to be bonded, by using a primer prepared mentioned above and a one-pack type urethane adhesive (WS-100, manufactured by Yokohama Rubber Co., Ltd.).

25 The bonding was conducted as follows. Namely, both samples to be bonded each having a width of 25 mm and a thickness of 5 mm were coated with the above-mentioned primer composition, and after drying, were coated with the adhesive, followed by bonding together, by overlapping them at a width of 10 mm, and allowed to stand at a temperature of 20°C and a relative humidity (RH) of 55% for 7 days.

30 The shear strength ( $\text{kgf/cm}^2$ ) and percent cohesive failure of adhesive of the bonded samples were measured by pulling both samples in the directions reverse to each other at a rate of 50 mm/min.

35 The kinds of samples to be bonded and phosphates used, and the measured results as to the shear strength



and percent cohesive failure of adhesive are listed in Table 1. In addition, the polypropylene and high solid paint for automobiles used as the samples are designated by "PP" and "Paint", respectively, in Table 1.

5

Table 1

No.	Example					Comparati ve Example	
	1	2	3	4	5	1	
	Polyisocyanate	100	100	100	100	100	100
	Component	750	750	750	750	750	750
15	Solvent	100	100	100	100	100	100
	Carbon Black	15	15	15	15	15	15
	Desiccant	0.3	0.3	0.3	0.3	0.3	0.3
20	Catalyst	15	15	15	15	15	15
	Polyurethane Resin	5	30	60	30	0	0
25	Phosphate a	0	0	0	0	30	0
	Phosphate b	PP	PP	PP	Paint	PP	PP
30	Sample	15	38	30	68	15	11
	Shear Strength [kgf/cm <sup>2</sup> ]	5	50	20	100	10	0
35	% Cohesive Failure of Adhesive						

As is clear from the results shown in Table 1, the hard-to-bond materials such as polypropylene and high solid paint for automobiles which have heretofore been incapable of being satisfactorily bonded with conventional primers can be effectively bonded together to exhibit good adhesion by the use of the primer composition according to the present invention.

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The effect of the present invention is clear from the aforementioned results.

5 As illustrated in detail above, hard-to-bond materials such as polyolefins and high solid paint can be bonded to exhibit adequate adhesion by the use of the primer composition according to the present invention. The primer composition of the present invention can therefore be suitably applied to, for example, the automobile industry, building industry, electronic and  
10 electric industry.

**WHAT IS CLAIMED IS:**

1. A primer composition comprising:
  - (a) at least one polyisocyanate component selected from the group consisting of 4,4'-diphenyl-methane diisocyanate, tolylene diisocyanate, xylene diisocyanates, hexamethylene diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, hydrogenated tolylene diisocyanates, hydrogenated xylene diisocyanates, isophorone diisocyanate, aromatic aliphatic polyisocyanates, aromatic polyisocyanates, triphenylmethane triisocyanates, and tris(p-isocyanatophenyl) thiophosphate, polymeric diphenylmethane diisocyanates and mixtures thereof; and
  - (b) at least one phosphate component selected from the group consisting of aluminum phosphate, zinc phosphate, and aluminum dihydrogentripolyphosphate, said phosphate is surface treated with Si, Zn or a mixture thereof.
2. A primer composition as claimed in claim 1, wherein said phosphate component is aluminum dihydrogentripolyphosphate.
3. A primer composition as claimed in claim 1, wherein the amount of the phosphate component is 5 to 100 parts by weight, based on 100 parts by weight of the polyisocyanate component.
4. A primer composition as claimed in claim 3, wherein the amount of the phosphate component is 30 to 60 parts by weight.
5. A primer composition as claimed in claim 1, wherein a solvent is further included in the composition.
6. A primer composition as claimed in claim 1, wherein the amount of the solvent is 500 to 1000 parts by weight, based on 100 parts by weight of the

polyisocyanate component.

7. A primer composition as claimed in claim 1, wherein a catalyst is further included in the composition.

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8. A primer composition as claimed in claim 7, wherein the amount of the catalyst is 0.1 to 1 part by weight, based on 100 parts by weight of the polyisocyanate component.

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9. A primer composition as claimed in claim 1, wherein a carbon black is further included.

10. A method for improving the adhesion to a hard-to-bond material by applying thereto a primer composition according to claim 1.

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