CA 2084295 C 2003/09/16

(11)(21) 2 084 295

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) **Date de dépôt PCT/PCT Filing Date**: 1991/05/23
(87) **Date publication PCT/PCT Publication Date**: 1991/12/12
(45) **Date de délivrance/Issue Date**: 2003/09/16
(85) **Entrée phase nationale/National Entry**: 1992/12/01
(86) **N° demande PCT/PCT Application No.**: EP 1991/000962
(87) **N° publication PCT/PCT Publication No.**: 1991/018956
(30) **Priorités/Priorities**: 1990/06/01 (P 40 17 802.1) DE;
1990/06/01 (P 40 17 801.3) DE;
1990/11/09 (P 40 35 680.9) DE

(51) **Cl.Int.^{5}/Int.Cl.^{5}** C09J 11/06, C09J 4/04, C09J 5/02
(72) **Inventeurs/Inventors**:
NICOLAISEN, HEINZ, DE;
REHLING, ANNETTE, DE
(73) **Propriétaire/Owner**:
HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, DE
(74) **Agent**: OGILVY RENAULT

(54) **Titre** : PRODUIT ADHESIF COMPOSE RENFERMANT UNE COLLE A BASE DE CYANOACRYLATE ET UN DERIVE IMIDAZOLE COMME AMORCE
(54) **Title**: COMBINATION PRODUCT FOR BONDING PARTS TO BE JOINED CONTAINING A CYANOACRYLATE ADHESIVE AND AN IMIDAZOLE DERIVATIVE AS PRIMER

(57) **Abrégé/Abstract**:

The use of certain imidazole derivatives such as 1-benzyl-2-methylimidazole, 1-benzylimidazole. 1-hydroxyethyl-2-phenyl- 4,5-dihydroimidazole, 2-phenyl-4,5-dihydroimidazole and N,N'carbonyldiimidazole as a primer with cyanacrylate adhesives to bond mouldings, particularly polyolefins, results in high-strength adhesive bonds even if time is long between the primer and the adhesive coating.

2084295

PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro

INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ^{5} **:**
C09J 4/00

A1

(11) Internationale Veröffentlichungsnummer: WO 91/18956

(43) Internationales Veröffentlichungsdatum: 12. Dezember 1991 (12.12.91)

(21) Internationales Aktenzeichen: PCT/EP91/00962

(22) Internationales Anmeldedatum: 23. Mai 1991 (23.05.91)

(30) Prioritätsdaten:
P 40 17 801.3 1. Juni 1990 (01.06.90) DE
P 40 17 802.1 1. Juni 1990 (01.06.90) DE
P 40 35 680.9 9. November 1990 (09.11.90) DE

(71) Anmelder: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstraße 67, D-4000 Düsseldorf 13 (DE).

(72) Erfinder: NICOLAISEN, Heinz ; Ossietzkyring 4, D-3000 Hannover 91 (DE). REHLING, Annette ; Gerrit-Engelke-Straße 12, D-3007 Gehrden 1 (DE).

(74) Gemeinsamer Vertreter: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN; TFP-Patentabteilung, Henkelstraße 67, D-4000 Düsseldorf 13 (DE).

(81) Bestimmungsstaaten: AT (europäisches Patent), BE (europäisches Patent), CA, CH (europäisches Patent), DE (europäisches Patent), DK (europäisches Patent), ES (europäisches Patent), FR (europäisches Patent), GB (europäisches Patent), GR (europäisches Patent), HU, IT (europäisches Patent), JP, KR, LU (europäisches Patent), NL (europäisches Patent), SE (europäisches Patent).

Veröffentlicht
Mit internationalem Recherchenbericht.
Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.

(54) Title: COMBINATION PRODUCT FOR GLUING JOINT PARTS, CONTAINING A CYANACRYLATE ADHESIVE AND AN IMIDAZOLE DERIVATIVE AS PRIMER

(54) Bezeichnung: KOMBINATIONSERZEUGNIS ZUM VERKLEBEN VON FÜGETEILEN, ENTHALTEND EINEN CYANACRYLAT-KLEBSTOFF UND EIN IMIDAZOLDERIVAT ALS PRIMER

(57) Abstract

The use of certain imidazole derivatives such as 1-benzyl-2-methylimidazole, 1-benzylimidazole, 1-hydroxyethyl-2-phenyl-4,5-dihydroimidazole, 2-phenyl-4,5-dihydroimidazole and N,N'carbonyldiimidazole as a primer with cyanacrylate adhesives to bond mouldings, particularly polyolefins, results in high-strength adhesive bonds even if time is long between the primer and the adhesive coating.

(57) Zusammenfassung

Die Verwendung von bestimmten Imidazolderivaten wie 1-Benzyl-2-methyl-imidazol, 1-Benzyl-imidazol, 1-Hydroxyethyl-2-phenyl-4,5-dihydroimidazol, 2-Phenyl-4,5-dihydro-imidazol und N,N'-Carbonyldiimidazol als Primer ergibt bei der Verklebung von Formteilen insbesondere aus Polyolefinen mit Cyanacrylat-Klebstoffen Klebverbindungen mit hoher Festigkeit auch bei langer Abdunstzeit.

A combination product for bonding parts to be joined containing a cyanoacrylate adhesive and an imidazole derivative as primer

This invention relates to a combination product for bonding parts to be joined of synthetic materials containing a cyanoacrylate adhesive and an imidazole derivative as primer and to the primer itself, to its use and to the bonding process.

It is known that moldings of synthetic materials, more particularly apolar materials, such as polyethylene, polypropylene, polybutylene, polyoxymethylene, polytetrafluoroethylene, polyurethane, polysilicones and the like can only be bonded to one another, after the surfaces of the moldings have been subjected to a special pretreatment, *cf.* Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1, page 254, Verlag Chemie Weinheim, 1985. Known pretreatments increase the surface energy of the moldings, generally through oxidation. Typical pretreatment methods include treatment with oxidizing flames, oxidizing substances or electrical discharges.

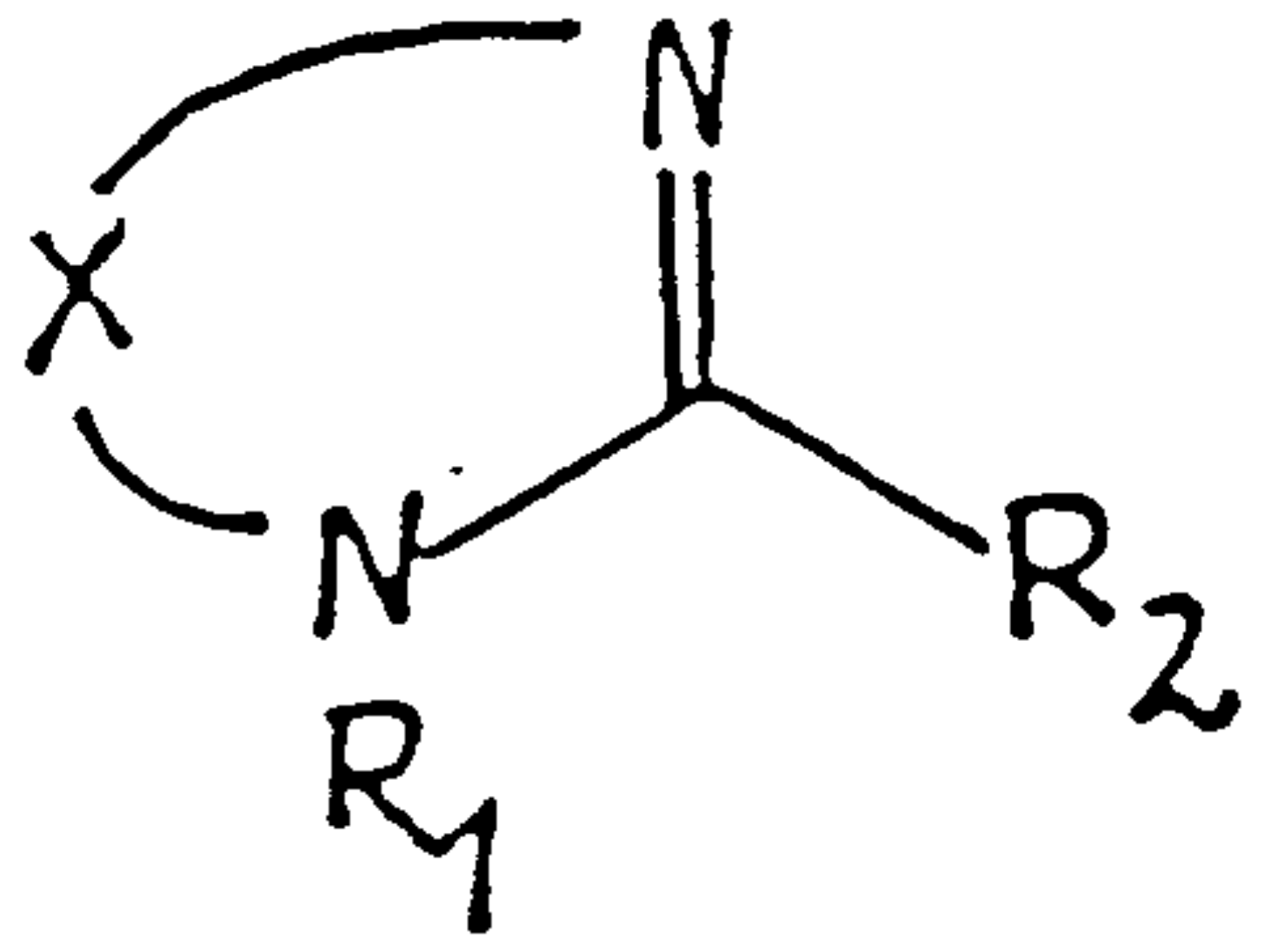
It is also known that the surfaces of apolar plastics which are to be bonded with cyanoacrylate adhesives can be pretreated with primers comprising solutions of certain active substances in suitable organic solvents. Thus, PCT WO 88/10289 describes the use of various diazabicyclo or triazabicyclo compounds in such solvents as acetone, methyl ethyl ketone, a chlorinated hydrocarbon or methanol as primers for the above-mentioned purpose. The primer solutions are applied to the surfaces to be bonded; after evaporation of the solvent, the cyanoacrylate adhesives are applied and the surfaces thus treated are joined. Other primers are primary aliphatic amines (EP-A 0 295 013), quaternary ammonium compounds (EP-A 339 448), derivatives of lutidine, picoline, pyiridine and 1-vinyl imidazole [C.A. 106:197637z, 197638a (1987)] and various quinoline and pyridine derivatives (JA 62/195071).

However, a major disadvantage of some of the primers mentioned above is that they accelerate curing of the cyanoacrylate adhesives without improving adhesion to the particular materials. On the contrary, distinctly poorer adhesion by comparison with non-pretreated surfaces is often obtained as a result of the spontaneous crosslinking. Another disadvantage of the primers known from PCT WO 88/10289 and EP-A 0 295 013 lies in the fact that subsequent coating with the cyanoacrylate adhesives has to be carried out as quickly as possible after application of the primer because otherwise the strength of the bond decreases. Another factor to be taken into consideration in the case of the well-known primer, vinyl imidazole, is that this compound is classified as extremely damaging to health.

Japanese patent application JP 02-45572 A describes a primer for cyanoacrylates of which the active substance is characterized by an imidazole ring. The following active substances are specifically mentioned: imidazole, 2-methyl imidazole, 2-ethyl-4-methyl imidazole, 1-hydroxyethyl-2-methyl imidazole, 2-aminobenzimidazole, 5-nitrobenzimidazole and N[(p-2-benzimidazole)-phenyl]-maleic acid imide. Higher shear strengths are obtained with primers containing these active substances than with primers containing dimethyl aniline, p-toluidine or diethyl amine. Nevertheless, the strengths achieved are still not high enough for many applications.

Accordingly, the problem addressed by the present invention was to improve the handling and performance properties of primers for cyanoacrylate adhesives and, more particularly, to eliminate the disadvantages mentioned above, i.e. to lengthen the storage time between application of the primer and application of the adhesive and, at the same time, to achieve high strength values.

The solution provided by the invention is based on the use of imidazole derivatives corresponding to general formula I



(I)

in which

R_1 is hydrogen, an alkyl group which may be unsubstituted or substituted by an HO group or an $(alkyl\text{-}O)_3$ Si group, the alkyl radical containing 1 to 4 carbon atoms, an arylalkyl group containing 7 to 10 carbon atoms or an imidazole-CO group and

R_2 is hydrogen, an alkyl, aryl or arylalkyl group containing up to 17 carbon atoms, with the proviso that one of the substituents R_1 or R_2 has an aromatic character,

X is one of the following groups:

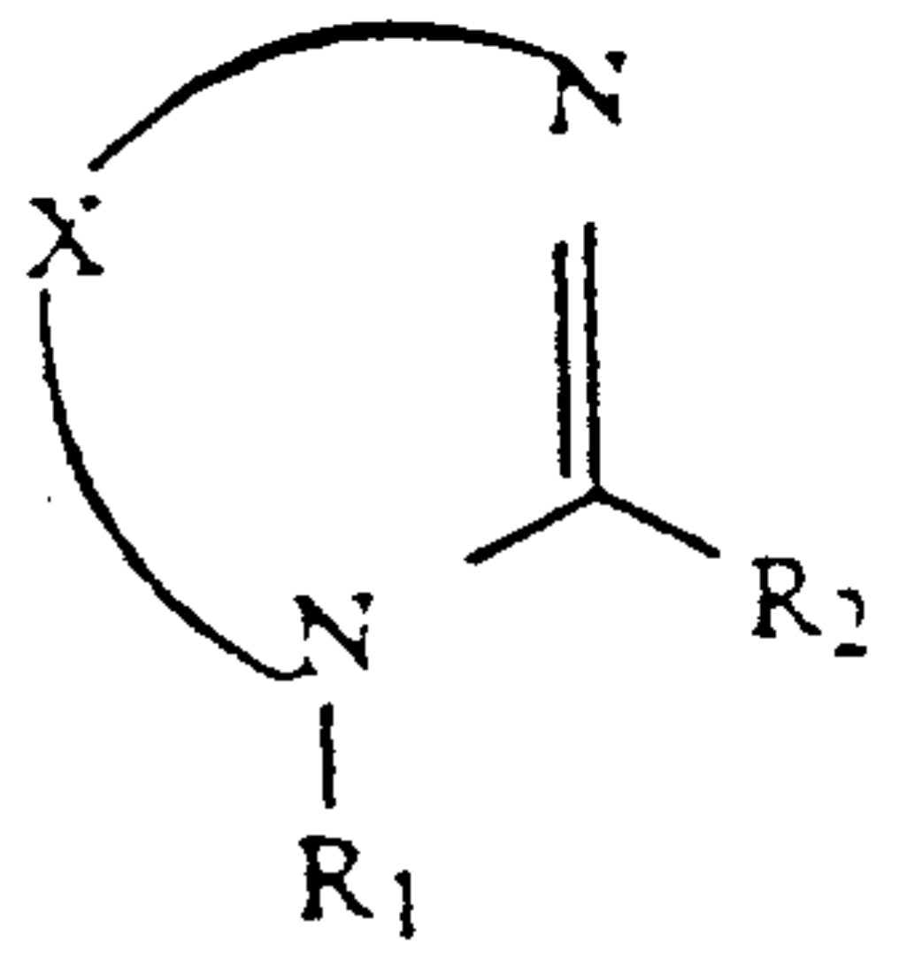
$-CH = CH-$ or

$-CR_3R_4-CR_5R_6-$

where R_3, R_4, R_5 and R_6 independently of one another represent hydrogen, an alkyl group containing from 1 to 4 carbon atoms or an arylalkyl group containing up to 17 carbon atoms.

Thus the invention provides in one aspect a process for bonding two synthetic plastic substrates, comprising the steps of:

(A) applying to the surface to be bonded of at least one of the substrates at least one imidazole derivative conforming to the general formula I:



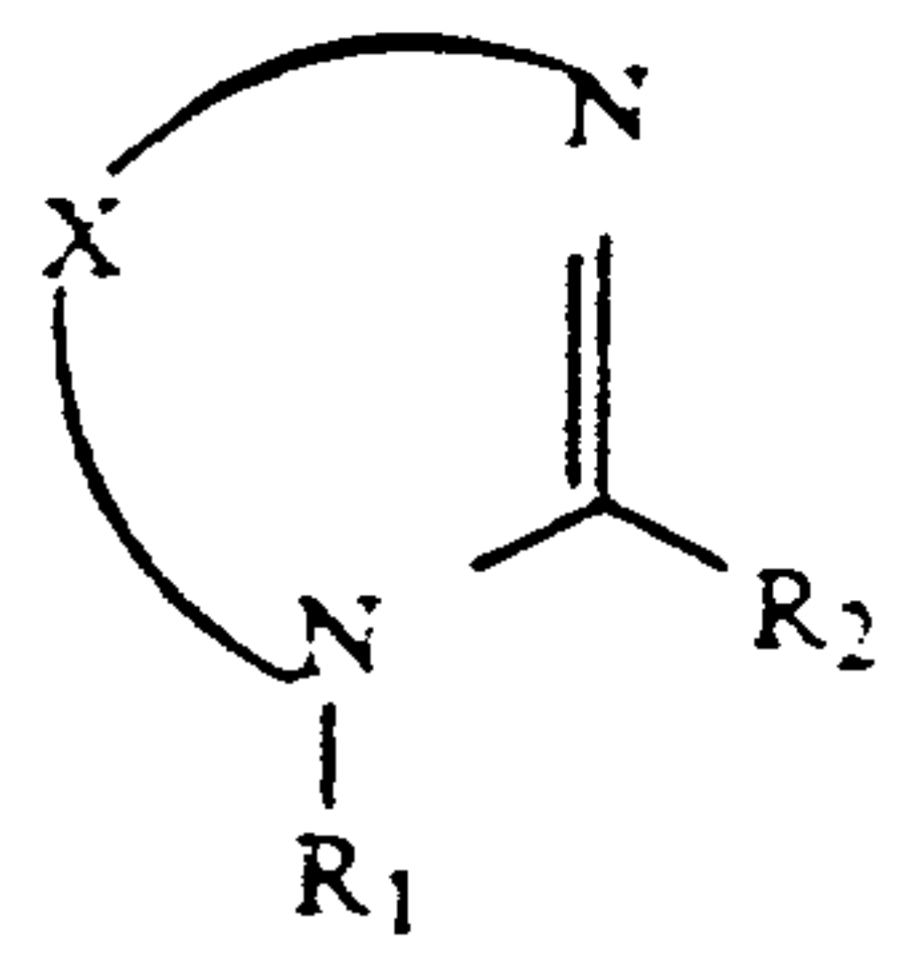
wherein (1) R_1 is selected from the group consisting of hydrogen; alkyl group that is unsubstituted or substituted with an HO group or with an $(alkyl-O)_3Si$ group, wherein the alkyl radical has 1 to about 4C atoms; arylalkyl groups with about 7 to about 10C atoms; and imidazole-CO groups, (2) R_2 is selected from the group consisting of hydrogen, and alkyl, aryl, and arylalkyl groups with up to about 17 carbon atoms, with the condition that one of the substituents R_1 or R_2 has an aromatic character, and (3) X is one of the groups -CH=CH- or $-CR_3R_4-CR_5R_6-$, wherein each of R_3, R_4, R_5 and R_6 independently of one another is selected from the group consisting of hydrogen, alkyl groups with 1 to about 4C atoms; and arylalkyl groups with up to about 17C atoms;

(B) subsequently applying to the surface prepared in step (A) a cyanoacrylate adhesive; and

(C) bringing the surface prepared in step (B) into contact with the other synthetic plastic surface to be bonded; and

(D) maintaining the surfaces contacted in step (C) in contact under sufficient pressure for a sufficient time to permit formation of an adhesive bond between the surfaces.

In another aspect, there is provided a composition of matter consisting essentially of from about 0.001 to about 5.0 w/o, based on the composition as a whole, of at least one imidazole derivative conforming to the general formula I:



wherein (1) R_1 is selected from the group consisting of hydrogen; alkyl group that is unsubstituted or substituted with an HO group or with an $(alkyl\text{-}O)_3Si$ group, wherein the alkyl radical has 1 to about 4C atoms; arylalkyl groups with about 7 to about 10C atoms; and imidazole-CO groups, (2) R_2 is selected from the group consisting of hydrogen, and alkyl, aryl, and arylalkyl groups with up to about 17 carbon atoms, with the condition that one of the substituents R_1 or R_2 has an aromatic character, and (3) X is one of the groups $-CH=CH-$ or $-CR_3R_4-CR_5R_6-$, wherein each of R_3, R_4, R_5 and R_6 independently of one another is selected from the group consisting of hydrogen, alkyl groups with 1 to about 4C atoms; and arylalkyl groups with up to about 17C atoms; and of an organic solvent that is chemically inert to the imidazole derivative and that will evaporate within about 24 hours at ambient temperature and pressure from a film no more than about 0.1 mm in thickness.

Under the general definition, a compound has a "aromatic character" when an electron sextet is present in an isocyclic or heterocyclic ring compound, as for example in benzene or imidazole.

Imidazole derivatives such as these provide for high-strength bonds with cyanoacrylate adhesives. Their strength surprisingly increases with the contact time of the primer and only diminishes after a relatively long time, more particularly after several hours. Accordingly, there is no longer any need to apply the cyanoacrylate adhesives and carry out bonding as soon as possible after treatment with the primer.

Preferred imidazole derivatives are those in which X = CR_3R_4-CR_5R_6-, more particularly 4,5-dihydroimidazole, which are also called imidazolines.

Where X is -CH = CH-, R_1 and R_2 preferably have the following meanings:

R_1 is an aryl group containing 7 to 10 carbon atoms or an imidazole-CO group and

R_2 is hydrogen or an alkyl group containing 1 to 4 carbon atoms.

More particularly, R_1 is a methyl or benzyl group and R_2 is hydrogen or a methyl group.

Where X is -CR_3R_4 - CR_5R_6-, R_1, R_2, R_3, R_4, R_5 and R_6 preferably have the following meanings:

R_1 is hydrogen or a hydroxyalkyl group,

R_2 is an aryl group or an arylalkyl group containing up to 17 carbon atoms and

R_3, R_4, R_5 and R_6 independently of one another represent hydrogen or an alkyl group containing 1 to 4 carbon atoms.

More particularly, R_1 is hydrogen or a hydroxyethyl group, R_2 is a benzyl or phenyl group and R_3, R_4, R_5 and R_6 are hydrogen.

A particularly advantageous imidazoline derivative for use in accordance with the present invention is 2-phenyl-2-imidazoline.

Typical examples of aryl or aralkyl groups which may form the substituents R_2 are phenyl, naphthyl, tolyl, xylyl, benzyl and naphthyl methyl groups. Typical examples of alkyl groups containing 1 to 17 carbon atoms, which may also form the group R_2, are methyl, ethyl, propyl, butyl, pentyl, heptyl, nonyl, undecyl, tridecyl, pentadecyl and heptadecyl groups; straight-chain alkyl groups are preferred. It is also possible to use technical mixtures of these 2-alkyl imidazole derivatives which contain alkyl groups as listed above varying in their chain length. Typical examples of alkyl groups containing 1 to 4 carbon atoms and aryl groups which may form the substituents R_3, R_4, R_5 and R_6 can be found in the above list.

The imidazole derivatives of general formula I to be used in accordance with the invention are particularly suitable for the pretreatment of polyoxymethylene, polyolefins, for example polyethylene, polypropylene and fluorinated polyethylenes, more particularly polytetrafluoroethylene, and also thermoplastic rubber compounds and silicone rubber compounds.

These materials may be bonded with typical cyanoacrylates, for example with cyanoacrylates corresponding to general formula II

$$H_2C=C(CN)-COOR^3 \qquad (II)$$

in which R^3 is an alkyl, alkenyl, cycloalkyl, aryl, alkoxyalkyl, aralkyl or haloalkyl group, more particularly a methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, allyl, methallyl, crotyl, propargyl, cyclohexyl, benzyl, phenyl, cresyl, 2-chloroethyl, 3-chloropropyl, 2-chlorobutyl, trifluoroethyl, 2-methoxyethyl, 3-methoxybutyl and 2-ethoxyethyl group.

The cyanoacrylates mentioned above are known to the expert on adhesives, *cf.* Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1, page 240, Verlag Chemie Weinheim (1985) and US-PS 3,254,111 and US-PS 3,654,340.

In another advantageous embodiment of the invention, the imidazole derivatives are used in solution in polar organic solvents which evaporate at room temperature and which are inert to the imidazole derivatives. Typical examples of such solvents are ketones, esters, alcohols, aliphatic and aromatic hydrocarbons and also halogenated hydrocarbons, including mixtures thereof. Particularly preferred solvents are those from the group consisting of ketones containing 3 to 8 carbon atoms, alkanols containing 1 to 4 carbon atoms and esters of acetic acid with alkanols containing 1 to 4 carbon atoms, for example acetone, methyl ethyl ketone, methanol, ethanol, propanol, butanol and also acetic acid ethyl, propyl and butyl ester.

In another advantageous embodiment of the invention, the imidazole derivatives are used in the form of a 0.001 to 5.0% by weight and, more particularly, 0.05 to 2.0% by weight solution. Solutions such as these can be applied to the surface to be treated in finely dispersed form by dip coating, spray coating, spread coating or other suitable methods. The contact time on the surface may be influenced by the rate of evaporation of the solvent or solvent mixture. Preferred solvents are those which, in addition to adequate dissolving power for the active substance, also provide for high stability thereof in the solution.

In addition, dyes or optical brighteners may be added to the primer solution to enable application to be better controlled. In this case, the presence of the primer after evaporation of the solvent can be detected by color contrasts or by suitable opto-electronic methods, for example luminescent tracers or UV lamps.

The invention relates not only to the use of at least one imidazole derivative corresponding to general formula I as primer for bonding parts to be joined of polyolefins, such as polyethylene or polypropylene, of fluorine-containing polymers or of thermoplastic rubber, but also to the primer itself, i.e. a composition containing at least one imidazole derivative corresponding to general formula I and a polar organic solvent which evaporates at room temperature.

The present invention also relates to a combination product for bonding parts to be joined of synthetic materials which, in addition to the primer, also contains a cyanoacrylate adhesive.

The present invention also relates to a process for bonding parts to be joined of synthetic materials with cyanoacrylate adhesives, imidazole derivatives corresponding to general formula I being used.

The invention is illustrated in the following with reference to preferred examples of embodiment.

Various imidazole compounds to be used in accordance with the invention were dissolved in a solvent selected from the group consisting of acetone, ethanol, propanol and a 1:1 (w/w) mixture of ethanol and ethyl acetate. In general, homogeneous solutions could be prepared in 30 minutes by shaking. Test strips of various materials measuring 100 x 25 x 3 mm were dipped into the solutions. The plastics used were polyethylene (Trovidur® PE, natur), polypropylene (Trovidur® PP, natur), polytetrafluoroethylene (Hostaflon® TF) and polyoxymethylene (DELRIN)*. After removal, the wetted samples were generally left for between 5 and 15 minutes for the solvent to evaporate. The pretreated test strips were then bonded with a commercially available cyanoacrylate adhesive based on ethyl cyanoacrylate [Sicomet® 8300 (a product of Sichel-Werke GmbH, Hannover, Federal Republic of Germany)]. After 2 to 3 drops of the adhesive had been applied to the pretreated surface, the adhesive was thoroughly distributed in a few seconds by application of a second test strip - which had also been treated with primer - with gentle sliding. After the freshly bonded parts to be joined had been exactly aligned to the necessary dimensions, they were pressed

*Trademark

together for 60 minutes in a fixing device. Slight surface unevenness could be leveled out and a favorable adhesive film thickness of 0.01 to 0.1 mm established in this way. The contact pressure required in practice is generally applied for only a few seconds to a few minutes.

The following imidazole derivatives were tested:

A: 1-Benzyl-2-methyl imidazole
B: N,N'-Carbonyl diimidazole
C: 1-Benzyl imidazole
1: 2-Phenyl-2-imidazoline
2: 1-Hydroxyethyl-2-phenyl-2-imidazoline
3: 2-Benzyl-2-imidazoline
4: 3-(4,5-Dihydroimidazol-1-yl)-propyl triethoxysilane
5: 3-(2-Imidazolin-1-yl)-propyl triethoxysilane.

After application of the primer solutions and the adhesive as described above and bonding at room temperature, the bonded test specimens were stored for 24 h at 20°C and then tested with a Wolpert TZM testing machine (50 kN) to determine the tensile shear strength of the bond at a crosshead speed of 100 mm/min. (in the case of POM: 25 mm/min.). The values set out in Table 1 below are average values of 5 individual measurements.

Table 1

Primer	Conc. of the acetone solution (% by weight)	Tensile shear strength [N/mm²] PE/PE1)	PP/PP2)	PTFE/PTFE3)	POM/POM4)
		The values in brackets were obtained after storage for 2 h			
a) Primer solution in acetone					
A	0.5	6.2	5.3	2.5	
B	0.2	4.1	6.2	3.0	
B	0.5	3.5	4.0	n.d.4)	
C	0.2	4.8	4.5	n.d.4)	
C	0.5	6.8	5.7	2.3	
C	1.0	5.1	4.5	2.0	
1	0.1	6.5	6.2	3.7	
1	0.5	7.2	6.5	4.0	
1	1.0	6.7	6.0	3.6	
b) Primer solution in ethanol/ethyl acetate (1:1)					
1	0.2	5.9	6.8	n.d.	6.5
1	0.5	7.2	7.4	n.d.	7.1
2	0.5	3.5	2.1	n.d.	n.d.
3	0.1	5.8(4.9)	6.2(5.0)	n.d.	5.8
3	0.2	6.0(5.2)	7.4(6.2)	n.d.	6.4
3	0.5	4.9(4.7)	5.2(5.5)	n.d.	n.d.
4	0.2	2.1	3.5	n.d.	n.d.
4	0.35	2.3	4.6	n.d.	n.d.
5	0.2	n.d.	5.8	n.d.	n.d.
Comparison	0	0.2	0.1	0	0.4

---

1) Polyethylene to polyethylene

2) Polypropylene to polypropylene

3) Polytetrafluoroethylene to polytetrafluoroethylene

4) Polyoxymethylene (POM) to polyoxymethylene

5) Not determined

The effects of the storage time after the pretreatment and after bonding were investigated in another series of tests. To this end, the test strips were wetted with the solution of the primer as described above, stored for various times and then bonded as described above. Concentrations of 0.2% by weight and 0.5% by weight imidazoline derivative in ethanol/ethyl acetate (1:1) were used. The tensile shear strengths were determined after storage of the bonds for 24 h. The results obtained are set out in Table 2 below.

Table 2

Primer	Concentration of the solution (% by weight)	Evaporation time (mins.)	Tensile shear strength (N/mm²) PE/PE	PP/PP
1	0.2	5	6.8	6.4
1	0.2	60	6.4	6.0
1	0.5	5	7.2	6.5
1	0.5	60	6.4	6.4
1	0.5	480	5.8	6.7
1	0.5	1440	5.3	6.0
1	0.5	2880	5.1	6.3
1	0.5	4320	5.2	6.1
A	0.5	5	6.5	7.2
A	0.5	60	5.8	7.0
A	0.5	480	4.8	6.5
A	0.5	1440	3.5	5.6
A	0.5	2880	3.1	5.4
A	0.5	4320	2.7	5.0
C	0.5	5	6.0	5.9
C	0.5	60	5.5	6.8
C	0.5	480	4.7	5.7
C	0.5	1440	3.6	4.3

In another series of tests, the test strips were wetted with the solution of the primer and left for 10 minutes for the solvent to evaporate, bonded as described above and stored for various times. The tensile shear strengths of the bonds were then determined as described above. The results obtained are set out in Table 3 below.

Table 3

Primer	Concentration of the acetone solution (% by weight)	Storage time after bonding (h)	Tensile shear strength (N/mm²)		
			PE/PE	PP/PP	PTFE/PTFE
1	0.5	8	5.5	4.5	2.8
1	0.5	24	7.2	6.5	4.0
1	0.5	168	7.5	6.7	4.0
Comparison	-	168	0.1	0.1	0.1

The influence of the solvents used was investigated in another test. To this end, the primer was dissolved in ethanol and in 2-propanol. The test strips were wetted with the solution. After an evaporation time of 10 minutes, the test strips were bonded as described above and the tensile shear strengths of the bonds were determined after storage for 24 h. The results obtained are shown in Table 4.

Table 4

Primer	Solvent	Conc. (% by weight)	Tensile shear strength (N/mm²)	
			PE/PE	PP/PP
1	Ethanol	0.2	6.8	6.0
1	Ethanol	0.5	7.3	6.7
1	2-Propanol	0.2	6.1	5.7
1	2-Propanol	0.5	6.4	6.0

In order further to evaluate the effect in the bonding of thermoplastic elastomers, a commercially available thermoplastic rubber (Santoprene® 101-64, a product of Monsanto, Gluvin-La Neuve, Belgium) was used. This material has the elastomer properties of a vulcanized rubber and the simple processing properties of a thermoplastic material. 100 x 10 x 3 mm test strips bonded with the commercially available cyanoacrylate adhesive just mentioned without primer pretreatment had a tensile shear strength of only about 0.1 N/mm² which corresponds to very poor adhesion. In this test, the primer solutions were again applied by brush. After the pretreatment, the test specimens were left for 10, 60 or 180 minutes for the solvent to evaporate. They were then bonded. The results are set out in Table 5.

Table 5

Primer	Solvent	Conc. (% by weight)	Evaporation time	Tensile shear strength (N/mm²)
A	Acetone	0.5	10	0.88
C	Acetone	0.5	10	> 1*
1	Acetone	0.2	10	> 1*
1	Acetone	0.5	10	> 1*
1	Acetone	0.5	60	> 1*
1	Ethanol	0.2	10	> 1*
1	Ethanol	0.5	60	> 1*
1	Ethanol	0.5	180	> 1*

* Material failure a few cm adjacent the bond

Thus, bond strength on thermoplastic elastomers can be increased several times by the primer to be used in accordance with the invention.

Comparison tests using a commercially available product and structurally the nearest known product

A major disadvantage of hitherto known primers is that their activity diminishes relatively quickly after application. After pretreatment with the primer and evaporation of the solvent, the parts to be joined have to be bonded relatively quickly with cyanoacrylate adhesive. In continuous assembly processes, this rapid reduction in activity can lead to distinct losses in the quality of bonding in the event of prolonged stoppage times and interruptions after application of the primer.

The following solutions were used for comparison:

1.) 1,8-Diazabicyclo-[5.4.0]-undec-7-ene
0.5% by weight in 1,1,2-trichloro-1,2,2-trifluoroethane (F 113)
see PCT WO 88/10289

2.) 1-Vinyl imidazole
0.5% by weight in ethanol/ethyl acetate (1:1)
see C.A. 106: 197637 z, 197638 a (1987)

The preparation of the solutions, pretreatment and bonding were carried out as described above.

The tensile shear strengths determined in dependence upon the storage time between application of the primer and bonding (= evaporation time) are shown in Table 6. Table 2 may be used for comparison.

The comparison tests show that the preferred primer according to PCT WO 88/10289 undergoes a fairly marked reduction in activity after an evaporation time of only > 1 hour before bonding to polyethylene and after an evaporation time of > 8 h before bonding to propylene.

1-Vinyl imidazole is even more unfavorable in its primer effect. Polyethylene has to be bonded <u>immediately</u>

after evaporation. After the pretreated plastics had been stored for only 5 minutes, the strength obtainable after curing of the adhesive was very poor. The behavior of polypropylene is slightly more favorable. However, after storage for 1 hour, the desired effect is again no longer present.

The active substances according to the invention represent a major improvement over known primers. This applies in particular to the primer according to the invention 2-phenyl-2-imidazoline. Even after 72 hours (= 4320 minutes), it shows high strength values of > 5 N/mm² on polyethylene. On polypropylene, the strength values obtained after storage of the pretreated test specimens for 72 hours are almost unchanged in relation to the initial data (> 6 N/mm²).

Table 6

Comparison Solution	Evaporation time (mins.)	Tensile shear strength [N/mm²] PE/PE[1]	PP/PP[2]
1	5	4.8	6.1
1	60	3.9	5.9
1	480	2.1	4.2
1	1440	1.4	2.0
1	2880	0.9	1.5
1	4320	0.8	1.2
2	1	5.7	5.8
2	5	1.3	6.1
2	60	0.8	1.3
2	480	0.6	0.6
2	1440	0.4	0.4

[1] PE/PE = polyethylene/polyethylene (Trovidur® PF, natur)

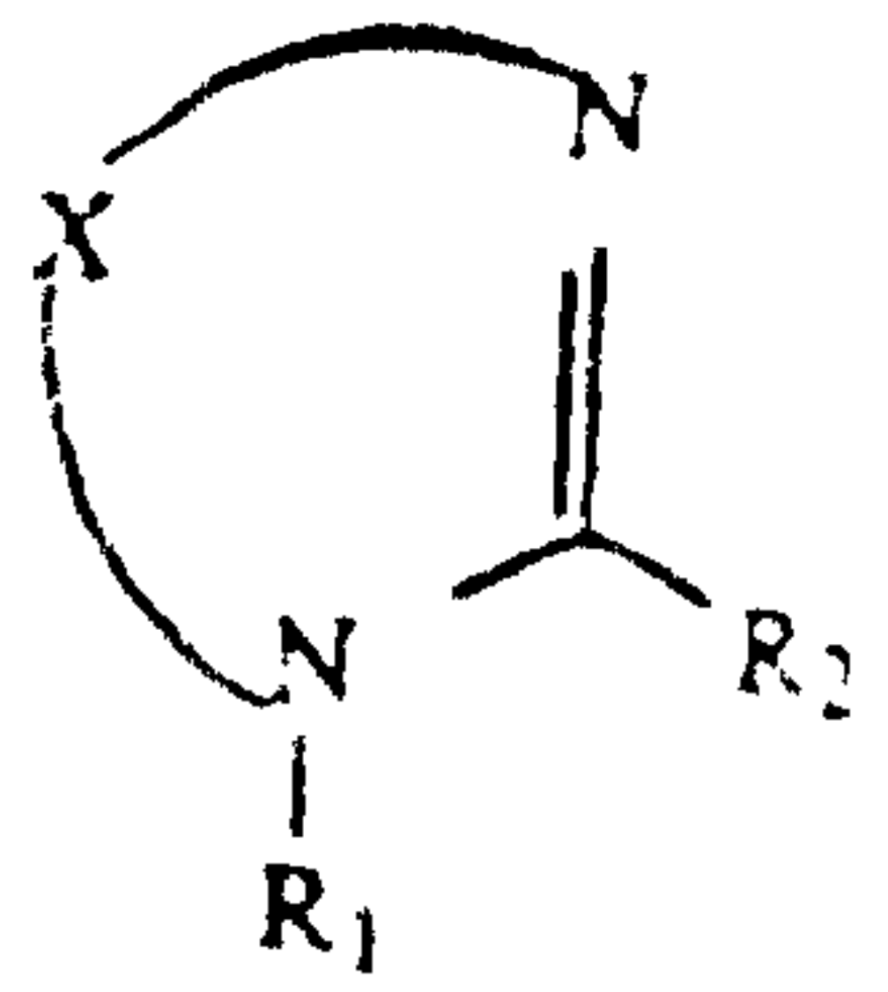
[2] PP/PP = polypropylene/polypropylene (Trovidur® PP, natur)

A primer specifically mentioned in JP 02-45572 A, namely imidazole, was used in another comparison test. A 0.5% by weight solution in acetone was applied to test strips of PE, PP and PTFE. After 15 minutes, the solvent had evaporated. Particulars of the further treatment can be found on pages 8 and 9. The following tensile shear strengths were obtained [in N/mm^2]:
2.0 for PE/PE, 2.5 for PP/PP and 1.5 for PTFE/PTFE.

Comparison with the results set out in Table 1 shows that the strengths are distinctly lower, i.e. are only about half as high.

CLAIMS

1. A combination product for bonding parts to be joined of synthetic materials containing a cyanoacrylate adhesive and an imidazole derivative as primer, characterized in that the primer contains at least one imidazole derivative corresponding to general formula I



in which

R_1 is hydrogen, an alkyl group which may be unsubstituted or substituted by an HO group or an (alkyl-O)$_3$ Si group, the alkyl radical containing 1 to 4 carbon atoms, an arylalkyl group containing 7 to 10 carbon atoms or an imidazole-CO group and

R_2 is hydrogen, an alkyl, aryl or arylalkyl group containing up to 17 carbon atoms, with the proviso that one of the substituents R_1 or R_2 has an aromatic character,

X is one of the following groups:

-CH = CH - or

$-CR_3R_4-CR_5R_6-$

where R_3, R_4, R_5 and R_6 independently of one another is selected from the group consisting of hydrogen, an alkyl group containing from 1 to 4 carbon atoms or an arylalkyl group containing up to 17 carbon atoms.

2. A combination product as claimed in claim 1, characterized in that

X represents -CH = CH-,

R_1 is an arylalkyl group containing 7 to 10 carbon atoms or an imidazole -CO group and

R_2 is hydrogen or an alkyl group containing 1 to 4 carbon atoms.

3. A combination product as claimed in claim 2, characterized in that R_1 is a benzyl group and R_2 is hydrogen or a methyl group.

4. A combination product as claimed in claim 1, characterized in that

X represents $-CR_3R_4 - CR_5R_6 -$,

R_1 is hydrogen or a hydroxyalkyl group,

R_2 is an aryl group or an arylalkyl group containing up to 17 carbon atoms and

R_3, R_4, R_5 and R_6 independently of one another represent hydrogen or an alkyl group containing 1 to 4 carbon atoms.

5. A combination product as claimed in claim 4, characterized in that R_1 is hydrogen or a hydroxyethyl group, R_2 is a benzyl or phenyl group and R_3, R_4, R_5 and R_6 are hydrogen.

6. A combination product as claimed in at least one of claims 1 to 5, characterized in that the imidazole derivatives are dissolved or suspended in polar organic solvents which evaporate at room temperature.

7. A combination product as claimed in claim 6 characterized in that the solvents are selected from the group consisting of ketones containing 3 to 8 carbon atoms, alkanols containing 1 to 4 carbon atoms and esters of acetic acid with alkanols containing 1 to 4 carbon atoms.

8. A combination product as claimed in at least one of claims 1 to 6 characterized by a 0.001 to 5.0% by weight solution of the imidazole derivatives.

9. A combination product as claimed in claim 8 characterized by a 0.05 to 2.0% by weight solution of the imidazole derivatives.

10. A primer for bonding parts to be joined of synthetic materials containing at least one imidazole derivative corresponding to general formula I as claimed in at least one of claims 1 to 9 in polar organic solvents which evaporate at room temperature.

11. A process for bonding parts to be joined of synthetic materials in which first an imidazole derivative and then a cyanoacrylate adhesive are applied to the surfaces to be joined, and bringing the surfaces to be joined into contact with each other and maintaining the surfaces in contact under sufficient pressure for a sufficient time to permit formation of an adhesive bond between the surfaces, characterized in that at least one imidazole derivative according to claims 1 to 10 is applied.

12. A process as claimed in claim 11, characterized in that imidazole derivatives according to claim 3 or 5 are applied.

13. A process as claimed in claim 11 or 12, characterized in that the imidazole derivatives are applied in solution in polar organic solvents which evaporate at room temperature.

14. A process as claimed in claim 13, characterized in that the solvents are selected from the group consisting of ketones containing 3 to 8 carbon atoms, alkanols containing 1 to 4 carbon atoms and esters of acetic acid with alkanols containing 1 to 4 carbon atoms.

15. A process as claimed in at least one of claims 11 to 14, characterized in that the imidazole derivatives are applied in the form of a 0.001 to 5.0% by weight solution.

16. A process as claimed in claim 15, characterized in that the imidazole derivatives are applied in the form of a 0.05 to 2.0% by weight solution.

17. The use of at least one imidazole derivative of general formula I according to at least one of claims 1 to 9 as primers for bonding parts to be joined of polyoxymethylene, polyolefins, fluorine-containing polymers, thermoplastic rubber, or silicone rubber.