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(54) Title: ALPHA-CYANOACRYLATE ADHESIVE SYSTEMS

(57) Abstract: An α-cyanoacrylate adhesive system, having an excellent fast setting property in the adhesion of hardly adhering materials and porous materials; having an excellent storage stability, even when a plastic material is used for at least a part of container for the adhesive composition, nozzle, cap and tube; using an α-cyanoacrylate adhesive composition comprising an α-cyanoacrylate and 0.05 to 5.0% by weight, based on said α-cyanoacrylate, of 12-crown-4-ether; and using a container for containing the adhesive composition, a nozzle and a cap, and optionally a tube for sending the adhesive composition to the nozzle, at least a part of said container, nozzle, cap and tube being made of a plastic material is provided.
DESCRIPTION

ALPHA-CYANOACRYLATE ADHESIVE SYSTEMS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an adhesive system of an α-cyanoacrylate adhesive composition.

More precisely, the invention relates to an adhesive system of an α-cyanoacrylate adhesive composition with a plastic container, a plastic nozzle, a plastic cap, or a plastic tube which is used to send the adhesive composition to the nozzle. Said adhesive has an excellent fast setting property and an excellent storage stability, and can be preferably used for the adhesion of hardly adhering materials such as acryl resins, chrome plating, nickel plating, FRP, Bakelite, thermoplastic elastomers (hereinafter, abbreviated as TPE), EPDM rubbers and the like, and porous materials such as papers, woods, leathers, ceramics and the like.

Description of Related Art

α-Cyanoacrylates easily cause anion polymerization by anionic active species, such as moisture, an alkaline material or the like, in a material to be adhered, or in the air, and so they found wide applications as instantaneous adhesives for rubbers, plastics, metals, glass and the like.

Conventional α-cyanoacrylate adhesives, however, do not have a sufficient fast setting property for the adhesion of
hardly adhering materials such as acryl resins, chrome plating, nickel plating, FRP, Bakelite, TPE, EPDM rubbers and the like, and porous materials such as papers, woods, leathers, ceramics and the like.

As a mean for removing this defect, a method in which a hardening accelerator is added to an \( \alpha \)-cyanoacrylate adhesive composition has been known. Various compounds have been attempted from 1975 to 1985 as hardening accelerators. For example, polyethylene glycol derivatives are disclosed in JP-A-54-28342 and calix-arenes are disclosed in JP-A-60-179482. In addition, JP-B-55-2238 discloses that crown ethers (15-crown-5-ether, 18-crown-6-ether and dicyclohexyl-18-crown-6-ether) are effective as hardening accelerators for the adhesion of porous materials such as papers, woods and the like.

On the other hand, however, another defect appeared that the storage stability of adhesives themselves is remarkably lowered when a hardening accelerator is added to an extent in which a sufficient fast setting property to a hardly adhering material is obtained.

Therefore, in order to storage an \( \alpha \)-cyanoacrylate adhesive composition containing a hardening accelerator for a long term, it is necessary to storage the adhesive composition filled in a metal container that is completely impermeable to water, or when the adhesive composition is filled in a plastic container permeable to water, it is necessary to store it in an atmosphere controlled to a low humidity. These are very inconvenient for the storage. Even if a metal container is
used, when one or both of nozzle and cap is of a water-permeable plastic material such as polyethylene, polypropylene or the like, moisture permeates through such part and hence lowering of storage stability can not be avoided. For example, moistening of the adhesive composition stayed in the inside of nozzle proceeds after applying the adhesive composition on a material to be adhered, causing rapid gelation, setting or the like. Upon next use, problems arise that the nozzle is blocked and the adhesive composition cannot be squeezed out from the container even when the adhesive composition in the container has no disorder (nozzle clogging). The nozzle clogging is frequent and has been one of great defects of the α-cyanoacrylate adhesives system. In addition, sometimes a problem arises that the whole of adhesive composition in a plastic container becomes hardened and the adhesive cannot be used. Improvement in these respects has been earnestly demanded.

In industrial adhesive applicators, the adhesive composition is introduced to a plastic nozzle as an outlet through a plastic tube, made of a water permeable material, having a narrow diameter. Also in this case, thickening, gelation or hardening due to moistening is liable to be occurred in a tube or nozzle during interruption or use in the summer. Improvement in this respect is also earnestly demanded.

Therefore, JP-A-62-100568 proposes an adhesive composition having the fast setting property and improved in stability during storage and use. The publication describes that the storage stability is improved as compared with a
conventional product when BF$_3$, SO$_3$ and 18-crown-6-ether or the like is added to 2-cyanoacrylate. Even if such adhesive composition is used, however, when a water-permeable plastic material is used for the nozzle or others, the nozzle clogging is liable to be occurred and therefore a satisfactory storage stability has not been attained. In other words, an adhesive in which a water-permeable plastic material is used for a nozzle, container or the like and which has an excellent fast setting property and an excellent storage stability has never been obtained.

**SUMMARY OF THE INVENTION**

The purpose of the invention is to provide an α-cyanoacrylate adhesive system having an excellent fast setting property in the adhesion of hardly adhering materials such as acryl resins, chrome plating, nickel plating, FRP, Bakelite, TPE, EPDM rubbers and the like, and porous materials such as papers, woods, leathers, ceramics and the like, and having an excellent storage stability, and no nozzle clogging when a plastic material is used for at least a part of the container for adhesive composition, nozzle, cap and tube.

As the result of extensive studies for solving these problems of the conventional adhesives, the present inventors have found the fact that, in the α-cyanoacrylate adhesive composition, when 0.05 to 5.0% by weight of 12-crown-4-ether is added to an α-cyanoacrylate, an excellent fast setting property in the adhesion of hardly adhering materials such as acryl resins, chrome plating, nickel plating, FRP, Bakelite,
TPE, EPDM rubbers and the like and porous materials such as papers, woods, leathers, ceramics and the like is obtained and setting during use or storage is extremely hard even if a plastic material is used for the container for adhesive composition, nozzle, cap or tube.

Therefore, the present invention provides an adhesive system which consists of an α-cyanoacrylate adhesive composition comprising an α-cyanoacrylate and 0.05 to 5.0% by weight, based on said α-cyanoacrylate, of 12-crown-4-ether, a container for containing said α-cyanoacrylate adhesive composition, a nozzle and a cap and, optionally a tube, at least a part of said container, nozzle, cap and tube being made of a plastic material.

DETAILED DESCRIPTION OF THE INVENTION

The invention is described below in detail.

The nozzle in the invention is connected to a container body of the adhesive composition, a tube or the like and the adhesive composition is flowed out through the nozzle.

Examples of the nozzle include one screwed in a container body, one welded to a container or others, one molded in one piece, or the like. Additionally, they include, for example, one attached to the tip of a pen-type container, one attached to the outlet for the adhesive of a tube used in an automatic applier, and the like.

The cap in the invention is one having a structure that can seal up the tip of nozzle or the container body for the adhesive composition. Examples thereof include generally
known caps of nozzle-covering type, those of container-covering type (double container) and the like.

The tube in the invention is one connecting the container for the adhesive composition or the like and the nozzle, and the adhesive composition is conveyed to the nozzle through this tube. This is used in automatic applier for adhesive composition or the like. Usually, a plastic tube having a narrow diameter is used.

At least a part or the whole of container for the adhesive composition, nozzle, cap and tube used in the adhesive system of the invention is made of a plastic material.

Examples of the plastic material used for the nozzle, cap, tube or the like include plastics such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyacetals, polycarbonates, polyethylene terephthalate, polytetrafluoroethylene and other fluorine resins, amorphous polyarylates and the like. Amongst them, polyethylene, polypropylene and polytetrafluoroethylene are preferred. They can be used independently or in a mixture or multi-layer structure, when required.

Examples of the plastic material for use in the container for the adhesive composition, i.e., the container for filling the α-cyanoacrylate adhesive composition, include, in addition to the above described plastics, poly-4-methylpentene-1, ionomers, polyvinylidene chloride, ABS resins, methacrylic resins, polyvinyl alcohol, cellulose plastics, TPE, epoxy resins, unsaturated polyester resins, phenol resins, urea-melamine resins, polyurethane resins,
silicone resins, polyimide resins, photo-curable resins, modified polyphenylene ethers, polybutylene terephthalate, polybutyne naphthalate, polyphenylene sulfide, polysulfones, polyetherimides, polyethersulfones, polyetherketones, polyamideimides, polyallylethernitriles, polybenzimidazole and so on.

In addition to the plastic materials, metallic materials such as aluminum and the like are usable. Particularly suitable materials for use in the container are polyethylene, polypropylene, polytetrafluoroethylene and aluminum.

They can be used independently or in a mixture or multi-layer structure, when required.

Suitable α-cyanoacrylate used in the invention include, for example, α-cyanoacrylate represented by the following general formula (2):

\[ \text{CN} \]
\[ \text{CH}_2\equiv\text{C} \quad \text{COOR} \]  

wherein R represents a saturated or unsaturated aliphatic or alicyclic group having 1 to 16 carbon atoms or an aromatic group.

Specific examples of the α-cyanoacrylate include esters of α-cyanoacrylic acid such as methyl, ethyl n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, octyl, neopentyl, cyclohexyl, ethylhexyl, dodecyl, allyl, methoxyethyl, ethoxyethyl, methoxypropyl, benzyl, phenyl, silyl, chloroethyl esters and the like. These α-cyanoacrylates can be used singly or in admixture of two or more.

The amount of 12-crown-4-ether to be added to the α-cyanoacrylate is 0.05 to 5.0% by weight based on the α-cyanoacrylate, and 0.1 to 3.0% by weight is a preferred range. When the amount is too small, the curing velocity is insufficient and, when the amount is too much, the storage stability becomes bad.

Furthermore, the inventors have found that the pH value of 10% by weight aqueous diluted solution of 12-crown-4-ether correlates with the performance of the adhesive composition, and that when 12-crown-4-ether having a pH value of 8.0 or less is selected for use, a superior performance can be obtained.

According to the above-described finding, it is preferred, in the present invention, that 12-crown-4-ether having a pH value of 8.0 or less in 10% by weight aqueous diluted solution is selectively used. It is more preferred that one having a pH value of 2.0 to 7.5 is selectively used.

In the α-cyanoacrylate adhesive composition used in the invention, the hardening accelerating effect of the 12-crown-4-ether can be more improved by adding a specific polyhydroxy compound. Preferred polyhydroxy compounds include polyhydroxy compounds represented by the following general formula (1):
wherein \( r \) represents an integer of 2 to 6; at least two hydroxyl groups are substituted on adjacent positions; \( Y \) represents hydrogen, straight chain or branched chain alkyl, alkoxy, carboxyl, alkoxy carbonyl or halogen; and \( s \) represents an integer of 0 to 4.

Specific examples include pyrogallol, catechol, di-t-butyl catechol, 1,2,4-trihydroxybenzene, hexahydroxybenzene, gallic acid, ethyl gallate, methoxyethyl gallate, dichlorogallic acid and the like. They can be used singly or in admixture of two or more, when required.

The amount of said polyhydroxy compound to be added is preferably 0.001 to 1.0% by weight, more preferably 0.005 to 0.5% by weight, based on the \( \alpha \)-cyanoacrylate.

It is preferred that an anionic inhibitor is comprised in the \( \alpha \)-cyanoacrylate adhesive composition. Suitable anionic inhibitor specifically includes sulfur dioxide, methanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, boron trifluoride diethyl etherate, \( \text{HBF}_4 \), trialkyl borate and the like. These compounds can be used singly or in combination of two or more according to the desired object. Particularly preferred combination is \( \text{HBF}_4 \) and sulfur dioxide. The range of amount of said anionic inhibitor to be used is preferably 0.1 to 100 ppm, more preferably 0.5 to 50 ppm, respectively.
The α-cyanoacrylate adhesive composition according to the invention may further comprise a thickener. Examples of the thickener includes homopolymer of a methacrylic acid ester, copolymers of different methacrylic acid esters, copolymers of methacrylic acid ester and acrylic acid ester, acrylic rubbers, polyesters, polyvinyl chloride, polystyrene, cellulose esters, polyalkyl α-cyanoacrylate, ethylene-vinyl acetate copolymer and the like. These may be used singly or in combination of two or more. Examples of specific compounds include polyalkyl methacrylates such as polymethyl methacrylate, polyethyl methacrylate, polypropyl methacrylate, polybutyl methacrylate and the like as the homopolymer of a methacrylic acid ester. Examples of compounds for use as a raw material for the copolymers of different methacrylic acid esters and the copolymers of methacrylic acid ester with acrylic acid ester include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate and the like. The homopolymer of an methacrylic acid ester, copolymers of different methacrylic acid esters, and copolymers of methacrylic acid ester with acrylic acid ester preferably has a weight average molecular weight of 100,000 to 2,000,000. The amount of the thickener to be contained is preferably 0.1 to 50% by weight, more preferably 1 to 30% by weight, based on the α-cyanoacrylate.

If necessary, the α-cyanoacrylate adhesive composition
according to the invention further comprises a radical inhibitor. Examples of the radical inhibitor include hydroquinone, hydroquinone monomethyl ether, pyrogallol, catechol, t-butylcatechol and the like. The amount of the radical inhibitor to be added is preferably 0.001 to 1.0% by weight, more preferably 0.005 to 0.5% by weight, based on the α-cyanoacrylate.

The α-cyanoacrylate adhesive composition used in the invention can be used with suitable addition of plasticizer, coloring agent, perfume, solvent, adhesive strength improving agent, inorganic filler and the like according to the desired usage, within a range in which the storage stability and fast setting property of the α-cyanoacrylate monomer is inhibited.

Examples of the plasticizer herein include dimethyl phthalate, diethyl phthalate, dibutyl phthalate, 2-ethylhexyl phthalate, diisodecyl phthalate, trimethyl acetylcitrate, triethyl acetylcitrate, tributyl acetylcitrate and the like.

As the inorganic filler, hydrophobic silica, hydrophilic silica and the like can be added as thixotropic property conferring agent.

The α-cyanoacrylate adhesive according to the invention has an excellent fast setting property in the adhesion of hardly adhering materials such as acryl resins, chrome plating, nickel plating, FRP, Bakelite, TPE, EPDM rubbers and the like, and porous materials such as papers, woods, leathers, ceramics and the like, hardly sets during storage and has an excellent storage stability despite a plastic material is used for a part or the whole of nozzle, cap, tube and container for the
adhesive composition.

The invention will now be described in more detail with reference to Examples, which should not be construed to limit the scope of the invention.

5 Measurements and evaluation in Examples were carried out according to the following methods:

<Set time (Measurement and evaluation of fast setting property)>

Measurement was carried out according to JIS K6861 using paper, Oregon Pine, EPDM rubber and acrylic resin as a material to be adhered (unit: second).

A shorter set time corresponds to an excellent fast setting property.

<Storage stability (Measurement and evaluation of storage stability for an adhesive composition contained in a container body)>

Into a polyethylene bottle (a tubular container having a length of 47 mm, a diameter of 11 mm and an outlet diameter of 5 mm, with a conic nozzle having a length of 31 mm, a bottom diameter of 11 mm and an outlet diameter of about 1 mm) was placed 2 g of an adhesive composition and gelling time was measured in an atmosphere of 60°C and 95% RH.

Exposure was carried out under heating and humidifying conditions in order to reproduce actual circumstance having humidity, using, as the container, a polyethylene bottle generally used as a container for α-cyanoacrylate adhesives composition.

The storage stability was evaluated with the following
scores according to days spent before gelation.

☺: equal to or more than 13 days; ○: 10 to 12 days;
△: 6 to 9 days; ×: equal to or less than 5 days.

<Nozzle-clogging resistance (Measurement and evaluation of storage stability for an adhesive composition in a nozzle)>

Into an aluminum tube (having a length of 45 mm, a diameter of 13 mm and an outlet diameter of 4 mm) was placed 3 g of an adhesive composition. After unsealing, a polyethylene nozzle (cone having a length of 25 or 31 mm, a bottom diameter of 12 or 13 mm and an outlet diameter of 1 mm) and a cap on the nozzle tip (a cone having a length of 32 or 35 mm, a bottom diameter of 14 or 15 mm) were attached.

Then composition was applied on a commercially available NBR test piece (1 × 25 × 100 mm, manufactured by Nippon Testpanel Co., Ltd.) for about 10 cm (0.05 g), contacting the nozzle tip thereon. After allowing the nozzle to stand for 30 minutes covering the nozzle tip with the cap, the composition was applied on a NBR in the same manner and the nozzle tip was covered. The nozzle was exposed in this condition to an atmosphere of 60°C and 95% RH and days were counted until the adhesive composition could not be squeezed due to setting of the composition stayed in the nozzle and clogging of the nozzle.

The nozzle-clogging resistance was evaluated with the following scores according to days spent before clogging.

☺: equal to or more than 10 days; ○: 7 to 9 days; △: 4 to 6 days; ×: equal to or less than 3 days.
Example 1

An adhesive composition was prepared by adding 10 ppm of HBF₄ and 10 ppm of SO₂ as anion inhibitors, 1,500 ppm of hydroquinone as a radical inhibitor and 4% by weight of PMMA (manufactured by Sumitomo Chemical Co., Ltd.) having a weight average molecular weight of 900,000 as a thickener to ethyl α-cyanoacrylate, followed by further addition of 1.2% by weight of 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution as a crown ether compound. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Example 2

An adhesive composition was prepared in the same manner as in Example 1 except that the amount of 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was changed to 0.3% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Comparative Example 1

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 15-crown-5-ether having a pH value of 7.6 in 10% by weight diluted aqueous solution (Tokyo Kasei's reagent) and its amount
was changed to 0.5% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Comparative Example 2

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 18-crown-6-ether having a pH value of 6.6 in 10% by weight diluted aqueous solution (Tokyo Kasei's reagent) and its amount was changed to 0.5% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and shown in Table 1.

Comparative Example 3

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 18-crown-6-ether having a pH value of 6.6 in 10% by weight diluted aqueous solution (Tokyo Kasei's reagent) and its amount was changed to 0.01% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Comparative Example 4
An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by t-butylcalix-6-arene having a pH value of 7.0 in 10% by weight diluted aqueous solution (Aldrich's reagent) and its amount was changed to 0.3% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Comparative Example 5

An adhesive composition was prepared by adding 10 ppm of BF₃ and 20 ppm of SO₂ as anion inhibitors, 500 ppm of hydroquinone as a radical inhibitor and 3% by weight of polymethyl methacrylate (manufactured by Sumitomo Chemical Co., Ltd.) having a weight average molecular weight of 900,000 as a thickener to ethyl α-cyanoacrylate, followed by further addition of 0.05% by weight of 18-crown-6-ether having a pH value of 6.6 in 10% by weight diluted aqueous solution (Tokyo Kasei's reagent) as a crown ether compound. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 1.

Example 3

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced
by 12-crown-4-ether having a pH value of 6.0 in 10% by weight diluted aqueous solution and its amount was changed to 0.5% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 2.

Example 4

An adhesive composition was prepared in the same manner as in Example 3 except that 10 ppm of HBF₄ and 10 ppm of SO₂ was replaced by 15 ppm of HBF₄ alone based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 2.

Example 5

An adhesive composition was prepared in the same manner as in Example 3 except that 10 ppm of HBF₄ and 10 ppm of SO₂ was replaced by 30 ppm of SO₂ alone based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 2.

Example 6

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 12-crown-4-ether having a pH value of 3.8 in 10% by weight
diluted aqueous solution and its amount was changed to 1.0% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 3.

Example 7

An adhesive composition was prepared in the same manner as in Example 6 except that 0.05% of pyrogallol was added based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 3.

Example 8

An adhesive composition was prepared in the same manner as in Example 4 except that PMMA having a weight average molecular weight of 900,000 was replaced by PMMA having a weight average molecular weight of 150,000 (manufactured by Sumitomo Chemical Co., Ltd.) and its amount was changed to 12% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 4.

Example 9

An adhesive composition was prepared in the same manner as in Example 4 except that PMMA having a weight average molecular weight of 900,000 was replaced by PMMA having a weight
average molecular weight of 70,000 (manufactured by Sumitomo Chemical Co., Ltd.) and its amount was changed to 23% by weight based on ethyl α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 4.

Example 10

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 12-crown-4-ether having a pH value of 7.5 in 10% by weight diluted aqueous solution, its amount was 1.2% by weight based on α-cyanoacrylate and methyl cyanoacrylate was used as α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 5.

Example 11

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 12-crown-4-ether having a pH value of 7.5 in 10% by weight diluted aqueous solution, its amount was changed to 0.3% by weight based on α-cyanoacrylate and isopropyl cyanoacrylate was used as α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 5.
Example 12

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 12-crown-4-ether having a pH value of 7.5 in 10% by weight diluted aqueous solution, its amount was changed to 2.0% by weight based on α-cyanoacrylate and methoxyethyl cyanoacrylate was used as α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 5.

Example 13

An adhesive composition was prepared in the same manner as in Example 1 except that 12-crown-4-ether having a pH value of 6.9 in 10% by weight diluted aqueous solution was replaced by 12-crown-4-ether having a pH value of 7.5 in 10% by weight diluted aqueous solution, its amount was changed to 0.5% by weight based on α-cyanoacrylate and ethoxyethyl cyanoacrylate was used as α-cyanoacrylate. The set time, storage stability and nozzle-clogging resistance of this adhesive composition were measured and the results are shown in Table 5.
Table 1

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Table 2

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Table 3

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CLAIMS

1. An adhesive system which consists of an α-cyanoacrylate adhesive composition comprising an α-cyanoacrylate and 0.05 to 5.0% by weight, based on said α-cyanoacrylate, of 12-crown-4-ether, a container for containing said α-cyanoacrylate adhesive composition, a nozzle and a cap and, optionally a tube, at least a part of said container, nozzle, cap and tube being made of a plastic material.

2. The α-cyanoacrylate adhesive according to claim 1, wherein the amount of 12-crown-4-ether is 0.1 to 3.0% by weight based on the α-cyanoacrylate.

3. The α-cyanoacrylate adhesive according to claim 1 or 2, wherein the 12-crown-4-ether has a pH value of 8.0 or less in 10% by weight aqueous diluted solution.

4. The α-cyanoacrylate adhesive according to any one of claims 1 to 3, wherein the α-cyanoacrylate adhesive composition further comprises a polyhydroxy compound represented by the following general formula (1):

\[
Y_S
\]
\[
(OH)_r
\]

wherein \( r \) represents an integer of 2 to 6; at least two hydroxyl groups are substituted on adjacent positions; \( Y \) represents hydrogen, straight chain or branched chain alkyl, alkoxy, carboxyl, alkoxy carbonyl or halogen; and \( s \) represents an integer of 0 to 4.
in an amount of 0.001 to 1.0% by weight based on the α-cyanoacrylate.

5. The α-cyanoacrylate adhesive according to any one of claims 1 to 4, wherein the α-cyanoacrylate adhesive composition further comprises an anionic inhibitor.

6. The α-cyanoacrylate adhesive according to claim 5, wherein the anionic inhibitor is a combination of HBF₄ and sulfur dioxide.

7. The α-cyanoacrylate adhesive according to any one of claims 1 to 6, wherein the α-cyanoacrylate adhesive composition further comprises a homopolymer of a methacrylic acid ester, copolymers of different methacrylic acid esters or copolymers of methacrylic acid ester and acrylic acid ester, as a thickener, which has a weight average molecular weight of 100,000 to 2,000,000, in an amount of 0.1 to 50% by weight based on the α-cyanoacrylate.