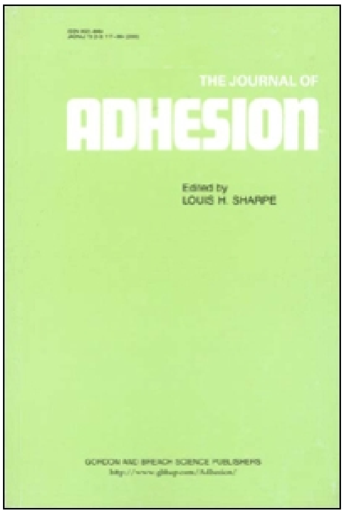

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Okamoto, Yoshihisa and Klemarczyk, Philip T.(1993) 'Primers for Bonding Polyolefin Substrates with Alkyl Cyanoacrylate Adhesive', The Journal of Adhesion, 40: 2, 81 — 91

To link to this Article: DOI: 10.1080/00218469308031275

URL: http://dx.doi.org/10.1080/00218469308031275

J. Adhesion, 1993, Vol. 40, pp. 81–91
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Printed in the United States of America.

Primers for Bonding Polyolefin Substrates with Alkyl Cyanoacrylate Adhesive

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(Received March 5, 1992; in final form July 27, 1992)

Polyolefins, such as polypropylene and polyethylene, are among the most commonly-utilized plastics in the world, but, because of their non-polar surfaces, are among the most difficult to bond with adhesives. A surface treatment is required before adhesive application to achieve good adhesion.

Alkyl cyanoacrylates are widely used instant adhesives, *e.g.* Super Glue®, for bonding a variety of substrates, such as metal, plastics, glass, wood, and leather. It would be desirable to bond polyolefins with these adhesives because of their availability and ease of use. Amines and ammonium carboxylates, possessing long alkyl chains, were evaluated as adhesion promoting primers for alkyl cyanoacrylate adhesives on polyolefins.

Among trialkyl amines, trialkylammonium carboxylates, and tetraalkylammonium carboxylates, trialkylammonium carboxylate primers produced an adhesive bond so strong that the failure occurred at the polyolefin substrate. Trialkylammonium carboxylate primers also demonstrated excellent performance retention over prolonged atmospheric exposure prior to application of the adhesive. Trialkyl amines and tetraalkylammonium carboxylates also promoted adhesion but lost maximum effectiveness on exposure to the atmosphere. The cause of the deterioration in amine primer effectiveness over prolonged exposure was identified to be trialkylammonium bicarbonate formation and/or diffusion of the primer into the polyolefin surface.

KEY WORDS primer; alkyl cyanoacrylate adhesive; polyolefin; trialkyl amines; trialkylammonium carboxylates; tetraalkylammonium carboxylates.

INTRODUCTION

Polyolefins, such as polypropylene and polyethylene, are widely-utilized plastics with surfaces that are non-polar and relatively inert. Because of these surface characteristics, adhesive bonding of these materials is difficult. Several surface treatment procedures, such as corona discharge, chlorochromate oxidation and flame treatment improve adhesion, but these methods are usually complicated, expensive, and are unable to treat the surface uniformly. A number of primer agents, which promote polyolefin adhesion with alkyl cyanoacrylate adhesives, have been reported in the patent literature to overcome these problems.[1]

Due to their fast fixture time, very high bond strengths, and ease of use, alkyl cyanoacrylate instant adhesives, *e.g.* Super Glue®, are widely used for bonding a variety of substrates such as plastics, metals, wood, glass, ceramics, and leather.[2] However, their utilization on polyolefins is limited without some surface treatment or primer application.

Novel primers which promote adhesion on polyolefins with alkyl cyanoacrylate adhesives were investigated. This report will discuss the results of that study.

EXPERIMENTAL

Stress-relieved polypropylene was obtained from Hüls America, Inc. as 0.5 cm sheets. The sheets were cut into 2.5 cm × 2.5 cm squares for adhesion test specimens.

Joint Strength Tests

Polypropylene specimens were cleaned in methylene chloride and dried with lab tissue. The primer was applied with a cotton swab to both PP specimens. The specimens were bonded by placing two drops of ethyl cyanoacrylate adhesive onto one PP specimen, and the second PP specimen was joined immediately. Finger tight pressure was maintained for *ca.* 10 seconds. Three test assemblies were bonded for each measurement, and all were aged overnight at room temperature. Joint strength was measured according to ASTM Test Method D4501 (Standard Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method).

Exposure Tests

a. Open Atmosphere—Primed PP specimens were placed in open, unfiltered air for the specified time before assembly with adhesive.

b. Dry Air—Primed specimens were placed in a desiccator immediately after the primer application. Specimens were removed at the specified time just prior to assembly with adhesive.

c. Moist, CO_2-Free Air—Moist, CO_2-free air was generated in a small chamber by passing compressed air through an aqueous sodium hydroxide solution. Primed specimens were placed in the chamber immediately after primer application. They were removed at the specified times just prior to assembly with adhesive.

d. Moist, CO_2-Free Nitrogen—The moist, CO_2-free nitrogen experiments employed an identical procedure to that for moist CO_2-free air, with the substitution of nitrogen for air.

Contact Angle Measurements

Contact angle measurements were performed on a Ramé-Hart NRL Contact Angle Goniometer in the open atmosphere. Polypropylene specimens were cleaned with methylene chloride and wiped dry.

The contact angles for the neat primers were measured by the application of one drop (*ca.* 15 μl) of primer onto clean PP, and allowing the drop to spread for 5 minutes. The contact angles were then measured.

For ECP contact angle measurements, clean PP specimens were dipped into primer solutions, and solvent was allowed to evaporate. The ECP contact angles were measured by placing one drop (*ca.* 15 μl) of ECP from the goniometer syringe onto the primed specimen. A minimum of 10 contact angle measurements were then obtained.

RESULTS AND DISCUSSION

Alkyl Cyanoacrylate Polymerization

Alkyl cyanoacrylate adhesives are extremely sensitive to base-catalyzed polymerization, as shown in Figure 1, and require stabilization by strong acid. As soon as the stabilizing acid is neutralized, any available anion or Lewis base initiates rapid polymerization to produce high molecular weight polymers. Hence, alkyl cyanoacrylates are considered to be instant adhesives.

Primer Criteria

In order to be an effective primer for this system, the priming agent should:

1. neutralize the stabilizing acid.
2. initiate polymerization of the alkyl cyanoacrylate adhesive.
3. be chemically stable.
4. not form a weak boundary layer.
5. remain on the surface for an extended period of time.

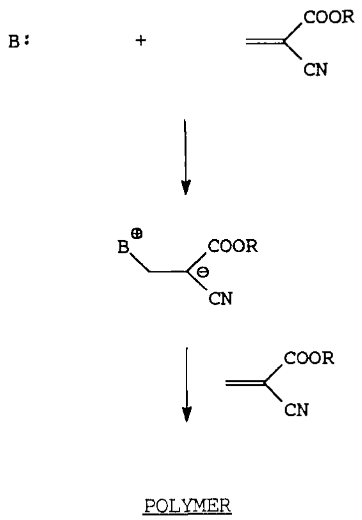


FIGURE 1 The polymerization of an alkyl cyanoacrylate initiated by a Lewis base, B:.

Alkyl Amine Primers

Amines containing one or more long alkyl chains appeared to satisfy the criteria outlined above. Stearyl amine (SA), distearyl amine (DSA), dimethylstearyl amine (DMSA), and distearylmethyl amine (DSMA) were examined as primers on polypropylene (PP) and polyethylene (PE). As shown in Figure 2, only tertiary amines possessing at least one long alkyl chain promote good adhesion on PP with ethyl cyanoacrylate adhesive. With the application of 0.10% DSMA primer, adhesive strength on PP was so strong, 23 MPa, that failure occurs at the PP substrate. Without primer, little or no adhesion was observed with ethyl cyanoacrylate adhesive.

A similar series of adhesion tests were also performed on PE and, again, tertiary amines possessing at least one long alkyl chain produced the highest adhesive strength, 14 MPa. Although the joint strength is lower than that measured on PP, failure still occurs at the PE substrate. Because the trends in adhesion-promoting effectiveness were similar for PP and PE, further testing was performed on PP alone.

Primer concentration is an important factor for adhesion promotion on PP, as

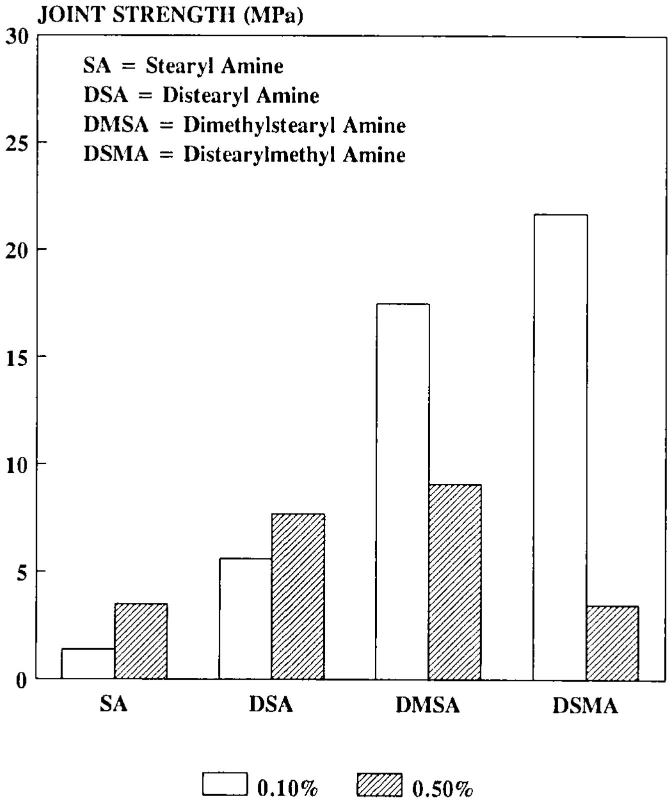


FIGURE 2 Effect of amine primer structure on polypropylene adhesion.

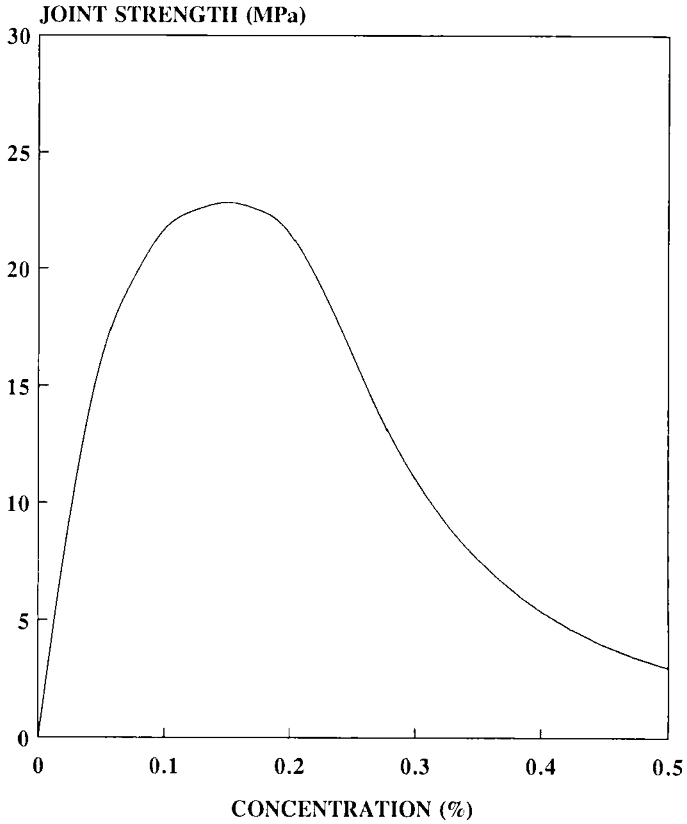


FIGURE 3 Effect of distearylmethyl amine concentration on polypropylene adhesion.

shown in Figures 2 and 3. DSMA primer at 0.10–0.25% levels in 2-propanol yielded maximum bond strengths.

Another factor that affects primer performance is the "open-time," which is the time that the primer is exposed to the atmosphere after application to the test specimen. As seen in Figure 4, the ability of DSMA to promote adhesion varied with concentration and open-time. At the lower concentration of 0.05%, initial adhesion was excellent, but it declined over a 24 hour open-time. In contrast, at the higher 0.50% concentration, initial adhesion was poor but improved dramatically after 24 hours of open-time. At the 0.10 and 0.25% concentrations, the performance of the DSMA primer was intermediate between the high and low concentrations.

One cause of the primer performance deterioration at lower concentrations over 24 hours could be ammonium bicarbonate formation from the reaction of the free amine with atmospheric moisture and carbon dioxide, as shown below. The presence of bicarbonate after

$$R_3N + CO_2 + H_2O \rightleftharpoons R_3NH^{\oplus}\ HCO_3^{\ominus}$$

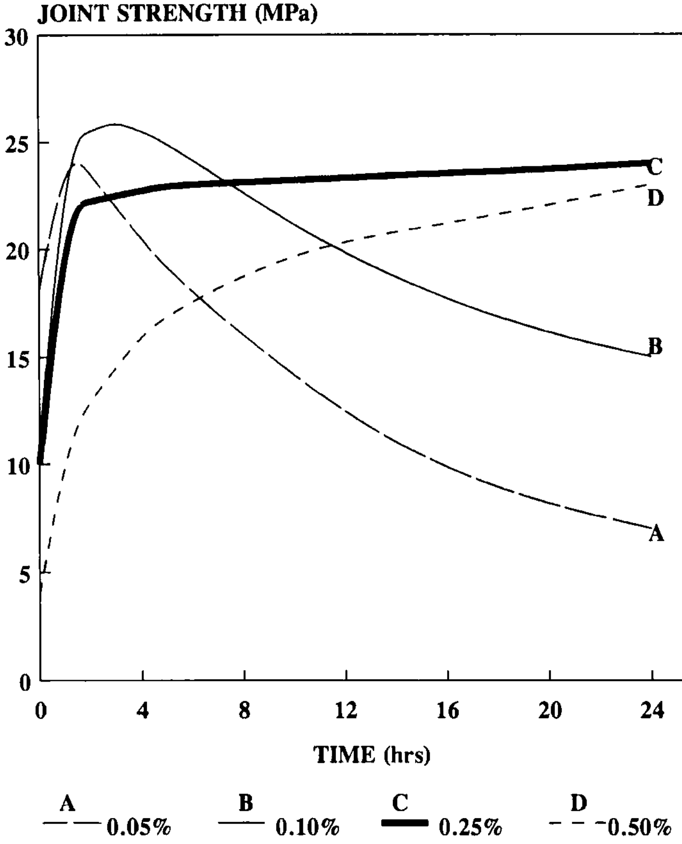


FIGURE 4 Effect of open time on polypropylene adhesion with four distearylmethyl amine concentrations.

a 24 hour open-time was confirmed by the appearance of weak, broad absorption bands at 1625 and 1730 cm^{-1} in the IR. By preventing bicarbonate formation in controlled atmospheres of dry air, moist CO_2-free air, and moist CO_2-free nitrogen, primer effectiveness can be maintained over 24 hours for all concentrations, as shown in Figure 5 for the dry air conditions. The joint strengths in moist CO_2-free air and moist CO_2-free nitrogen are virtually identical to those shown in Figure 5.

The results in dry air and moist CO_2-free air also indicate that the oxidation of the amine to the N-oxide is not a factor in the performance deterioration.

Another cause of the primer performance variation could be diffusion of the primer into the PP substrate. Research conducted by Garton[3] demonstrated that when triphenylphosphine is the primer, it diffused into the PP. Further studies are currently underway to determine if this is occurring with amine and ammonium carboxylate primers.[4]

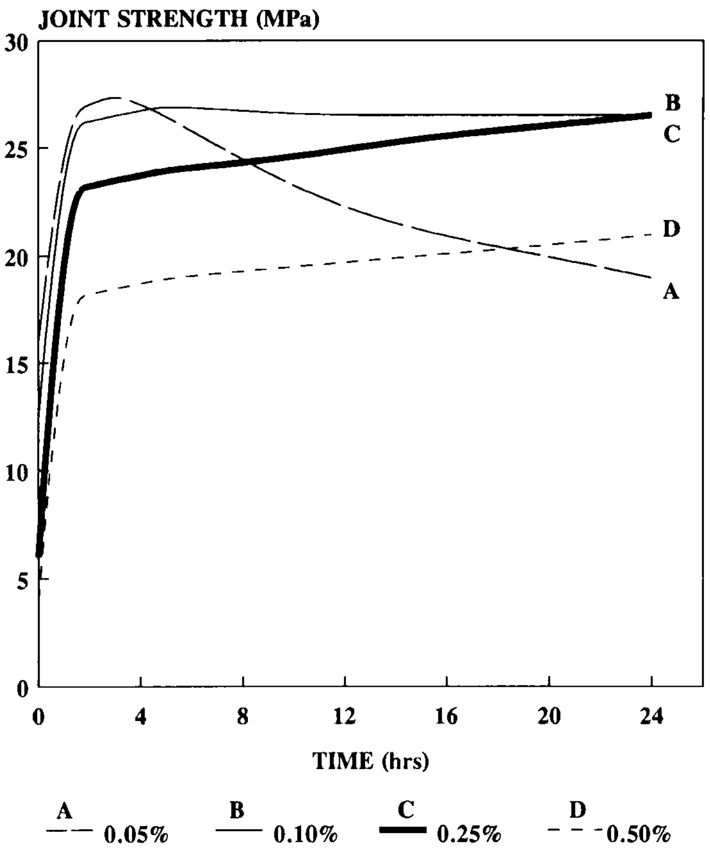
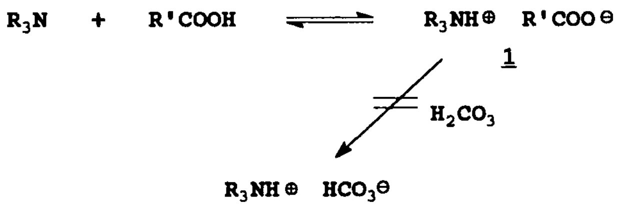


FIGURE 5 Effect of distearylmethyl amine concentration and open-time on polypropylene adhesion in dry air.

Trialkylammonium Carboxylate Primers

Because bicarbonate formation could be one reason for primer performance deterioration, trialkylammonium carboxylates, *1*, which preclude bicarbonate formation, were examined as primers.



As shown in Figure 6, among distearylmethylammonium acetate, butyrate, and stearate, only the stearate primer maintained its performance over a 24 hour open-time.

The decline in primer performance for the acetate and butyrate could be attributed to free amine formation and subsequent reaction with carbon dioxide and water to yield the bicarbonate. As shown in Figure 7, an IR study clearly demonstrates the difference between the butyrate and the stearate on prolonged atmospheric exposure. The IR of the stearate clearly shows the carboxylate absorptions at 1718 and 1569 cm^{-1}, even after a 24-hour atmospheric exposure. For the butyrate, the carboxylate absorptions disappeared after 20 minutes, and only the IR absorptions for the free amine are apparent. If a trialkylammonium carboxylate is to prevent bicarbonate formation, the starting carboxylic acid must possess a long alkyl chain and a very low vapor pressure.

Tetraalkylammonium Carboxylate Primers

Tetrabutylammonium acetate, *2*, structurally similar to trialkylammonium carboxylates, generated bond strengths of 21 MPa in primer tests with ethyl cyanoacrylate

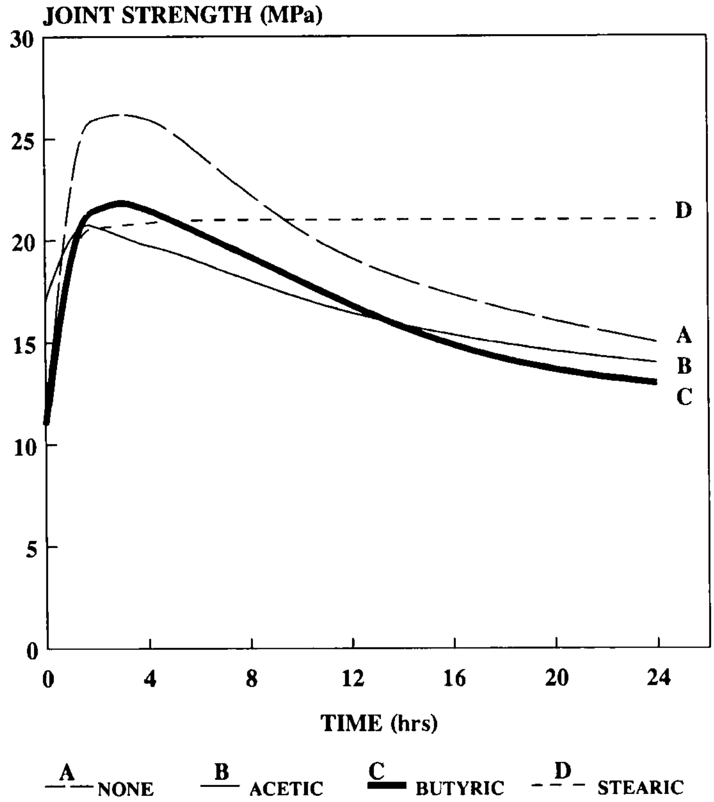


FIGURE 6 Effect of distearylmethylammonium carboxylate formation on polypropylene adhesion.

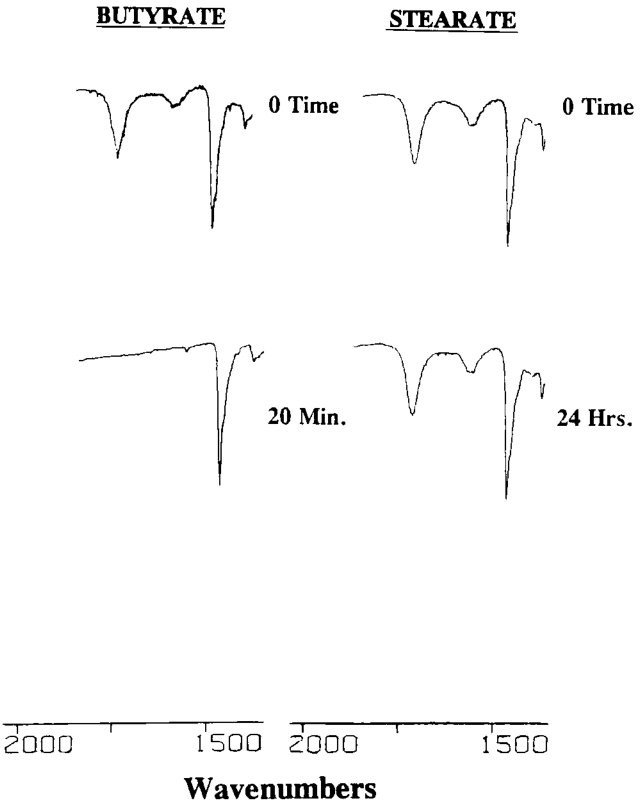


FIGURE 7 IR of distearylmethylammonium butyrate and stearate over time.

adhesive, when the specimens were assembled immediately. However, adhesion promotion declined to 6 MPa within one hour of open-time.

$$(C_4H_9)_4N^{\oplus} \quad CH_3COO^{\ominus}$$

2

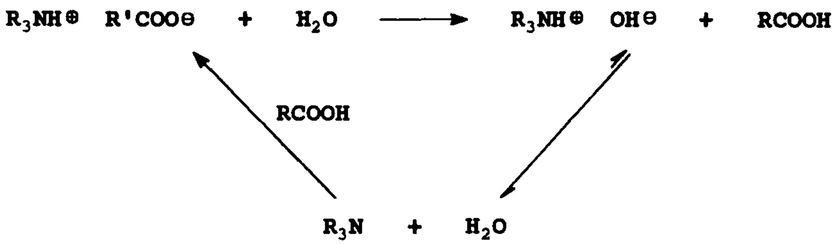
Tetradecylammonium stearate, which possesses long alkyl chains, was then examined, but adhesion promotion was found to be poor, regardless of concentration, after a 24-hour open-time.

The reduction of tetraalkylammonium carboxylate effectiveness as a primer over time could be attributed to the reaction of the carboxylate with water to form tetraalkylammonium hydroxide, as shown below.

$$R_4N^{\oplus}\ R'COO^{\ominus} \quad + \quad H_2O \quad \longrightarrow \quad R_4N^{\oplus}\ OH^{\ominus} \quad + \quad R'COOH$$

Tetradecylammonium hydroxide was utilized as a primer to test this hypothesis, and its use resulted in only 5 MPa of joint strength on PP.

In contrast, trialkylammonium carboxylates cannot form stable ammonium hydroxides in the same manner.



The proximity of the carboxylic acid favors the carboxylate formation over the bicarbonate. Because trialkylammonium carboxylates resist chemical changes on atmospheric exposure, they are superior to the tetraalkylammonium carboxylate as primers.

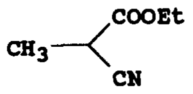
Primer Wettability

The ability of the primer to wet the substrate surface and the ability of the alkyl cyanoacrylate to wet the primed surface could be factors for the mechanism of adhesion promotion.

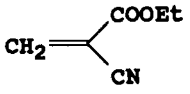
Firstly, contact angle studies of two primers on PP were conducted. The contact angle measurements for diazabicycloundecene and tetradecylammonium stearate are summarized in Table I.

Contrary to expectations, primer wettability on the surface does not seem to be critical for optimal adhesion promotion.

Secondly, the contact angle of ethyl 2-cyanopropionate (ECP), substituted for the reactive ethyl cyanoacrylate (ECA), was measured



ECP



ECA

on the primed PP surface. The results for various primers are summarized in Table II.

These data again indicate that adhesive wettability on the primed surface does not seem to be critical for good adhesion promotion.

Overall, the contact angle data do not provide a simple correlation between the primer effectiveness and the ability of the primer to wet the substrate surface or the adhesive to wet the primed surface. The chemical composition and environmental stability of the primer appear to be more important for good adhesion promotion on polyolefin substrates with alkyl cyanoacrylate adhesives.

TABLE I
Contact angles of primer on PP

Primer	Contact angle	Adhesion strength (MPa)
Diazabicycloundecene	39 ± 2	21
Tetradecylammonium Stearate	17 ± 2	12.6

TABLE II
Contact angles of ECP on primed PP

Primer	ECP Contact angle	Adhesion strength (MPa)
None	37 ± 3	—
Diazabicycloundecene	36 ± 3	21
Distearylmethyl amine	41 ± 2	23
Distearylmethylammonium stearate	48 ± 2	22
Tetrabutylammonium stearate	31 ± 2	12

CONCLUSIONS

1. Primers for alkyl cyanoacrylate adhesives can effectively promote adhesion on polyolefin substrates. Little or no adhesion is observed when a primer is absent.
2. Trialkylammonium carboxylates, possessing long alkyl chains, are effective adhesion promoters for alkyl cyanoacrylate adhesives on polyolefin plastics, such as polypropylene. They maintain their adhesion promotion ability after 24 hours of atmospheric exposure.
3. Trialkyl amines with long alkyl chains also perform well, but their effectiveness is limited to shorter periods of atmospheric exposure.
4. Some tetraalkylammonium carboxylates are good primers only if the specimens are assembled immediately after primer application.
5. Deterioration of amine primer performance over prolonged exposure could be due to bicarbonate formation and/or diffusion of primer into the substrate.

Acknowledgments

The authors wish to acknowledge the work of Ms. S. Levandoski and Ms. S. Hanlon on this project and Loctite Corporation for permission to publish this paper.

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