ThreeBond TECHNICAL NEWS

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New Instant Adhesives

Introduction

Initially tackled by Goodrich Corporation, USA, its efforts to develop instant adhesives date back to 1949. Eastman Chemical Company, a subsequent developer, achieved an instant adhesive suitable for actual use. The development of instant adhesives was triggered by an accidental discovery by an engineer while testing a new product. As the engineer was attempting to measure the refractive index of a newly synthesized cyanoacrylate, this organic compound became firmly attached to the prism of the refraction meter. Thereafter, researchers focused attention on cyanoacrylate's adhesive properties. In 1959, the first viable product was marketed under the name “Eastman 910.” Since that time, many companies around the world have sought to modify and commercialize instant adhesives.

Our own efforts to develop instant adhesives began in 1969. Currently in the ThreeBond 1700 Series, we release a product lineup offering various characteristics.

Just like it sounds, instant adhesives are adhesive agents that bind adherends rapidly – within several to several tens of seconds. Due to their quick curing, versatility, and convenience, they have been used in a wide range of applications ranging from domestic to industrial. In recent years, issues such as global warming, fossil fuel resource depletion, and enhancement of working area are highlighted and companies have shifted their production lines to a streamlined architecture without furnaces to achieve higher energy efficiency. This trend has led to the re-evaluation of the one-part solvent-free instant adhesives that offer instant and powerful bonding strength, and demand for such products is rising steadily year after year worldwide.

This issue will introduce two products developed as a result of extensive and continuous research at our company to meet the demand for products with simpler workability.

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1 Advantages and Disadvantages of Instant Adhesives

The primary component of instant adhesives are 2-cyanoacrylate esters, whose molecules feature polarized electron distributions, with some areas having high and other parts low electron densities, due to the presence of strong electrophilic groups such as the cyano group and carbonyl group. Instant adhesives can easily mount nucleophilic attacks, even on weak bases such as water (humidity), to promote anion polymerization.

This anion polymerization is extremely sensitive and progresses rapidly in a linear fashion, producing excellent fast-curing properties. But the linear structure of the polymer chain also results in less desirable features, such as low heat resistance.

Table 1 lists the properties of instant adhesives.

Table 1. Advantages and disadvantages of instant adhesives

Advantages		Disadvantages	
1	Quick curing at room temperature	1	Low water and humidity resistance
2	One-part, solvent-free agent	2	Blooming
3	High bonding strength	3	Low heat resistance (80°C)
4	Capable of bonding a wide range of materials	4	Low impact resistance
5	Capable of bonding materials of different types	5	Rigid cured product
6	Low materials use	6	Unsuitable for high-gap filling adhesion

Although the fast-curing property of instant adhesives is most recognized, their capacity to bind together nearly any material is another noteworthy advantage. The instant adhesives are used in various purposes, from domestic, industrial, to medical applications.

On the other hand, instant adhesives have certain disadvantages listed in Table 1. They generally offer poor water and humidity resistance, making them unsuitable for use under wet or humid conditions. Blooming also makes them less useful for applications that must require good appearance. Aslo, since the cured products with instant adhesives are hard and brittle, they offer less impact resistance, peeling resistance, or thermal cycle resistance.

The selection of appropriate monomers and the study of additives are gradually eliminating these disadvantages. Blooming may be avoided by using cyanoacrylate ester at low vapor pressure (ThreeBond 1720D series) or by using instant adhesives to which light-curing properties have been added (ThreeBond 1770E Series). This permits instant curing of any projecting parts using ultraviolet or visible light. These light-curing instant adhesives also enable high-gap filling adhesion through a combination of humidity curing and light curing processes. Alloying with the addition of rubber components to the adhesive agent improves impact resistance, peeling resistance, and thermal cycle resistance.

2 Ultra-Fast Curing Instant Adhesive - ThreeBond 7700 Gold Label Series

2-1 ThreeBond 7700 Gold Label Series

By now, the rapid curing of instant adhesives is common knowledge and is the key feature that can be imagined when he/she hears the term. But for materials that are difficult to bond, such as porous or acidic materials like paper or wood, EPDM, and polyacetal, the rapid bonding expected by customers cannot be achieved. In addition, environmental issues and energy efficiency concerns have led to demands for highly efficient production lines in factories. One strategy to achieve this goal is the design of high-speed production lines. One-part instant adhesives that cure quickly at room temperature improve workability and are well-suited to such applications. Thus, the development of products with such properties may contribute to environmental conservation.

In response to such trends, we have decided to return to the starting line with respect to instant adhesives and to promote the development of products that commit to “bond in a fraction of a second.” We have focused our efforts on improving the purity and quality at the monomer level to create instant-binding adhesives, successfully developing the potent, ultra-fast curing adhesives as the ThreeBond 7700 Gold Label Series.

2-2 Characteristics of the ThreeBond 7700 Gold Label Series

Table 2 lists the properties and characteristics of the ThreeBond 7700 Series (“ThreeBond” will be referred to as “TB” hereinafter).

Figure 1 illustrates the set time for TB7781 as a representative example; Table 3 lists the bonding strengths to various adherends.

Table 2. Properties and characteristics of the TB7700 Series

Advantages			Unit	Standard	Ultra-Fast Curing Series			Test Method
				TB7741	TB7781	TB7782	TB7784	
Properties	Appearance		-	Clear, pale yellow	Clear, pale yellow	Clear, pale yellow	Clear, pale yellow	3TS-201-01
Properties	Viscosity		mPa • S	2	2	15	160	3TS-210-01
Properties	Specific gravity		-	1.05	1.05	1.05	1.06	3TS-213-02
Characteristics	Coefficient of linear expansion (0-100°C)		/°C	81 - 124	79 - 116	77 - 121	83 - 135	3TS-501-05
Characteristics	Glass transition point (DMA E'')		°C	110	107	109	118	3TS-501-04
Characteristics	Hardness		-	D80	D80	D82	D82	3TS-215-01
Characteristics	Dielectric breakdown voltage		kV/mm	30	30	27	26	3TS-406-01
Characteristics	Volume resistivity		Ω • m	1.5×10^{14}	1.6×10^{14}	1.8×10^{14}	1.5×10^{14}	3TS-401-01
Characteristics	Surface resistivity		Ω	1.2×10^{15}	6.2×10^{14}	1.0×10^{15}	1.8×10^{15}	3TS-402-01
Characteristics	Dielectric constant	1MHz	-	3.51	3.93	3.85	6.08	3TS-405-01
Characteristics	Dielectric constant	1kHz	-	3.05	3.42	3.33	5.29	3TS-405-01
Characteristics	Dissipation factor	1MHz	-	0.037	0.037	0.038	0.037	3TS-405-01
Characteristics	Dissipation factor	1kHz	-	0.028	0.028	0.029	0.028	3TS-405-01

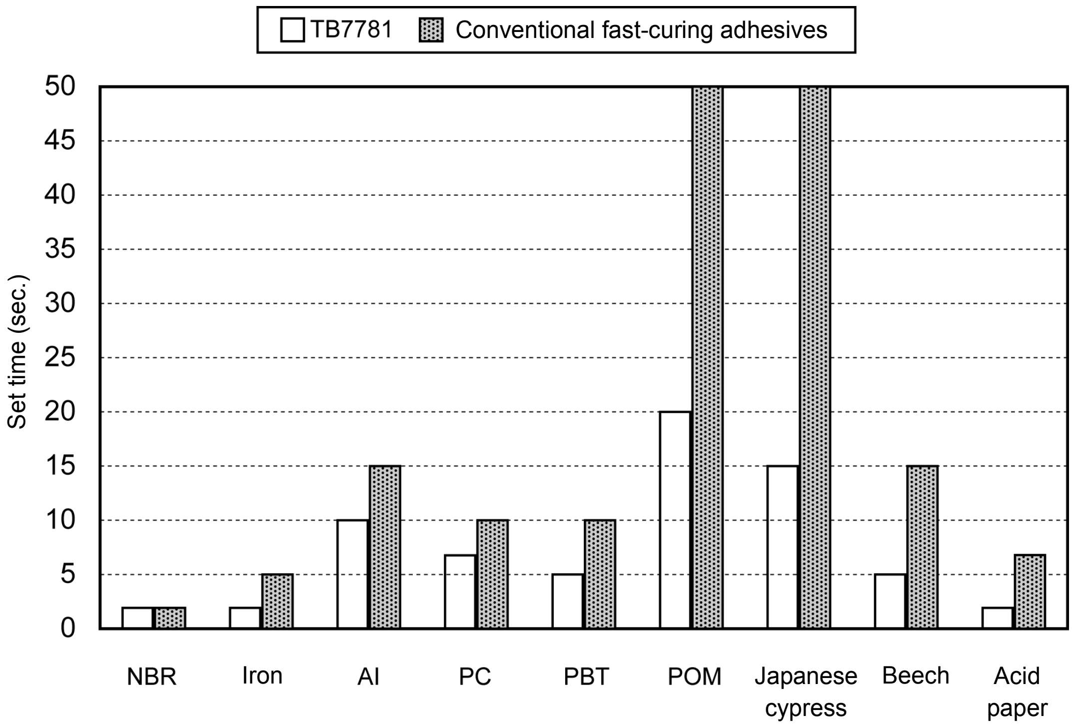

Figure 1. Time required for TB7781 to set on various adherends (3TS-220-04)

Table 3. Bonding strength of TB7781 to various adherends

Adherend type	Tensile lap shear strength (MPa)
Iron	14.0
Aluminum	14.9
SUS	12.2
Brass	9.0
Copper	12.7
Nickel	13.3
Zinc chromate	7.5
Hard vinyl chloride	3.0
PC (Polycarbonate)	6.9*
Phenol	10.5*
6-Nylon	8.1*
6,6-Nylon	13.1*
Noryl	9.3*
ABS (Acrylonitrile-butadiene-styrene resin)	6.2*
Glass epoxy	19.2
PBT (Polybutylene terephthalate)	4.3
PET (Polyethylene terephthalate)	10.5*
PPO (Polyphenylene oxide)	8.0
PPS (Polyphenylene sulfide)	1.9
HIPS (High impact polystyrene)	4.4*
Acrylic	7.6*
Polyacetal	1.2
NR (Natural rubber)	0.4*
CR (Chloroprene rubber)	0.6*
NBR (Acrylonitrile butadiene rubber)	0.8*
SBR (Styrene-butadiene rubber)	1.7*
EPDM (Ethylene propylene dieneterpolymer)	0.8*
Acid paper	-*
Balsa wood	1.8*
Lauan wood (single panel)	8.8*
Japanese cypress	11.2*

* indicates material failure.

As shown in Table 2, we currently market one standard product and three ultra-fast curing products, which have different viscosities. All products offer excellent curing properties and relatively good shelf lives through thorough removal of impurities.

Figure 1 illustrates the comparison between set times of our ultra-fast curing product and conventional product. Except for materials such as NBR for which short set times had been achieved by conventional products, TB7781 (ultra-fast curing type) clearly succeeds in reducing the set time for nearly all adherends, with significant reductions seen in difficult-to-bond materials such as POM (polyacetal) and acidic and porous materials such as wood and paper. This is due to the high monomer purity of TB7781, which is caused by less cure inhibition and faster polymerization. Since the adhesive cures before it seeps into the pores, the product provides excellent adhesive properties, even with materials like wood. As shown in Table 3, except for materials with strengths higher than the adhesive, such as metals, all adherends indicate material failure (the failure of the adherend material itself instead of the bonding area, which indicates strong adhesion), which suggests that the adhesive will exhibit adequate bonding strength with a wide range of materials.

2-3 Applications for the ThreeBond 7700 Gold Label Series

TB7700 Gold Label Series provides unprecedented ultra-fast curing properties not available in conventional products and they are expected to contribute to increasing the efficiency of various production lines. Their high curing speed will not only speed up the line, but may help reduce fixing jigs and the curing space required.

Their adoption will help realize the reduction in both the energy consumed upon production and the total cost required for operation of the line. Some major examples of their application are as follows:

(1) General parts that require rapid adhesion
(2) Adhesion of porous materials
(3) Temporary fixation for epoxy resin or acrylic resin adhesives that require time or fixation jigs for curing

Photo 1. Appearance of the TB7700 series
(Semi-transparent containers with light-blocking effect, that the remaining amount can be checked)

3 High Humidity-Resistant Instant Adhesive – The ThreeBond 1757

3-1 ThreeBond 1757

As shown in Table 1, instant adhesives also have several disadvantages, including poor water and humidity resistance. To date, few methods have been reported to improve these characteristics. In practice, there are few instant adhesive products that offer excellent resistance to high temperatures and high humidity conditions or in water immersion. Instant adhesives also provide low heat resistance (up to 80°C), which makes them unsuitable for applications requiring durability. Due to these drawbacks, their instant bonding capacity and superior workability have not been fully demonstrated. However, through dedicated effort and investigations of methods for improving water and humidity resistance, we have successfully developed a high humidity-resistant instant adhesive that has a higher reliability by blending a certain reactive monomer. The following section discusses this development in detail.

3-2 ThreeBond 1757 Characteristics

Table 4 lists the properties and characteristics of TB1757. As with conventional instant adhesives, TB1757 provides excellent adhesive performance for various substrates.

Figures 2 and 3 show the humidity resistance of TB1757. Figure 2 presents the results of tensile lap shear strength measurements (tension test specimen speed: 10 mm/min) conducted on aluminum plates bonded at 25°C, 50% RH, and cured for 72 hours under the same condition, which were then immersed in an 80°C, 95% RH thermo-hygrostat bath for the specified duration before measuring at room temperature.

Figure 3 shows the results of peeling resistance measurements of a bond between iron with a cationic electrodeposition coating and SEBS (styrene- (ethylene-butylene) -styrene block copolymer) formed at 25°C, 50% RH, and cured for 72 hours under the same conditions. The assembly was then immersed in an 80°C, 95% RH thermo-hygrostat bath for the specified duration before measuring the 90° peeling resistance (tension speed of test specimen: 50 mm/min) at room temperature. The “TB1757/TB1797E” in the graph indicates that a primer (TB1797E: primer dedicated for the TB1750 Series) was applied to the SEBS surface before adhesion.

Table 4. TB1757 properties and characteristics

Items			Unit	TB1757	Test method
Monomer	Appearance		-	Clear, pale yellow liquid	3TS-201-01
Monomer	Main component		-	2-cyanoacrylate ester	—
Monomer	Viscosity		mPa • s	1200	3TS-210-01
Monomer	Set time	NBR	sec	20	3TS-220-04
Monomer	Set time	Iron	sec	30	3TS-220-04
Copolymer	Tensile lap shear strength	Iron	MPa	19.2	3TS-301-11
Copolymer	Tensile lap shear strength	Aluminum	MPa	16.0	3TS-301-11
Copolymer	Tensile lap shear strength	ABS	MPa	8.1*	3TS-301-11
Copolymer	Tensile lap shear strength	PC	MPa	5.1*	3TS-301-11
Copolymer	Tensile lap shear strength	NBR	MPa	0.8*	3TS-301-11
Copolymer	Tensile lap shear strength	EPDM	MPa	0.8*	3TS-301-11
Copolymer	Coefficient of linear expansion (0-100°C)		10^{-6}/°C	90 - 140	3TS-501-05
Copolymer	Glass transition point temperature Tg		°C	122	3TS-501-04
Copolymer	Dielectric breakdown voltage		kV/mm	24.0	3TS-406-01
Copolymer	Volume resistivity		Ω • m	15×10^{13}	3TS-401-01
Copolymer	Surface resistivity		Ω	1.5×10^{14}	3TS-402-01
Copolymer	Dielectric constant	1MHz	-	2.87	3TS-405-01
Copolymer	Dielectric constant	1kHz	-	3.37	3TS-405-01
Copolymer	Dissipation factor	1MHz	-	0.029	3TS-405-01
Copolymer	Dissipation factor	1kHz	-	0.047	3TS-405-01

* indicates material failure. See Table 3 for definitions of acronyms used in the table.

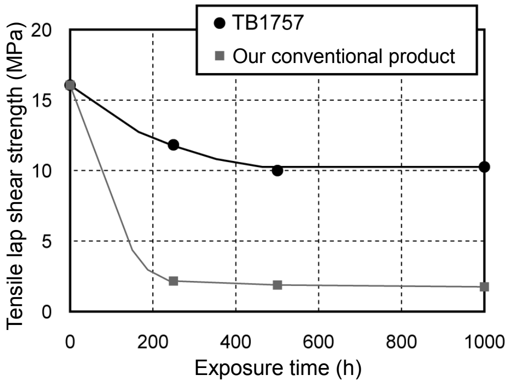

Figure 2. Humidity resistance at 80°C, 95% RH (for aluminum/aluminum bond)

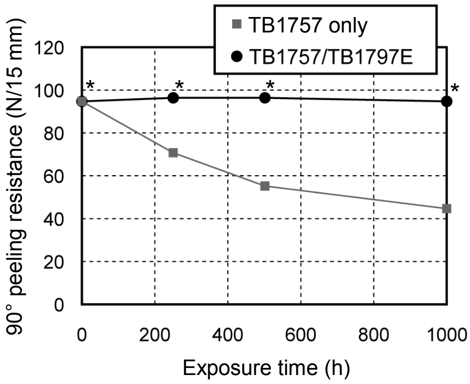

Figure 3. Humidity resistance at 80°C, 95% RH (for the cationic electrodeposited iron/SEBS bond)

The asterisks (*) in the graph indicate observed material failure.

Figure 2 shows that the bonding strength of common instant adhesive (our conventional product) drops rapidly over time, with near-total loss of bonding strength after 200 hours. In contrast, the TB1757, although indicating a certain decline in bonding strength, continues to maintain bonding strength exceeding 10 Mpa, even after aging of (80°C, 95% RH) x 1,000 hours.

Figure 3 also shows that TB1757 has excellent humidity and heat resistance, even when bonding between heterogeneous adherends such as cationic electrodeposited iron and SEBS. Rubber elastomers such as SEBS contain various additives and are known to bloom or bleed under high humidity and heat conditions, and then tend to reduce bonding strength due to degradation of the bonding surface. However, the extent of degradation is markedly lower with TB1757 than with conventional products. Pre-treating the SEBS surface with TB1797E, a primer dedicated for the TB1750 Series, further suppresses degradation. Bonding under dry conditions produces excellent humidity and heat resistance, with no observed reductions in bonding strength, even under conditions of 80°C, 95% RH.

Figure 4 shows the water resistance of TB1757. Tensile lap shear strength measurements (tension speed of test specimen: 10 mm/min) were performed on aluminum plates bonded at 25°C, 50% RH and cured for 72 hours under the same condition. These were then immersed in water at different temperatures for specified duration and dried for 24 hours at room temperature before measurement.

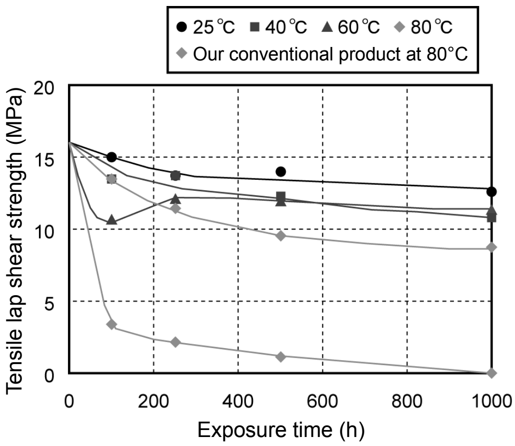

Figure 4. Water Resistance

Figure 4 shows that while common adhesive (our conventional product) lose nearly all bonding strength after 100 hours of immersion in water at 80°C, the TB1757 retains a bonding strength above 8 MPa even after 1,000 hours.

Results from Figures 2, 3, and 4 show that the TB1757 demonstrates sufficient resistance to wet conditions under which conventional products fail.

Finally, Figure 5 shows the heat resistance of TB1757. Iron plates were bonded at the respective temperatures and tests of tensile lap shear strength were performed at the same temperature. Figure 6 shows the results of tensile lap shear strength measured at 120°C of specimens aged for the specified duration at 120°C. Figure 7 shows the results of tensile lap shear strength measurements for iron plates after they were bonded, exposed to heat cycles alternating between -40°C x 1 hour and 120°C x 1 hour for the specified number of cycles, and cooled back to room temperature.

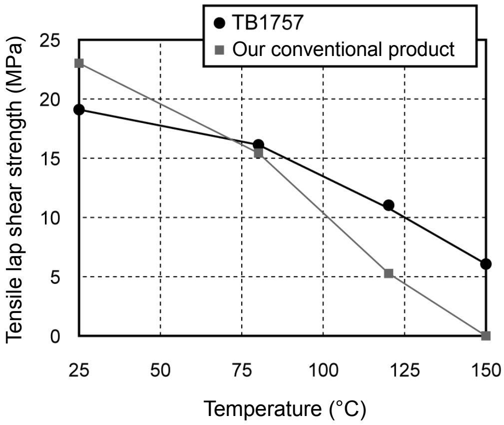

Figure 5. Heat resistance (bonding strength upon initial heating)

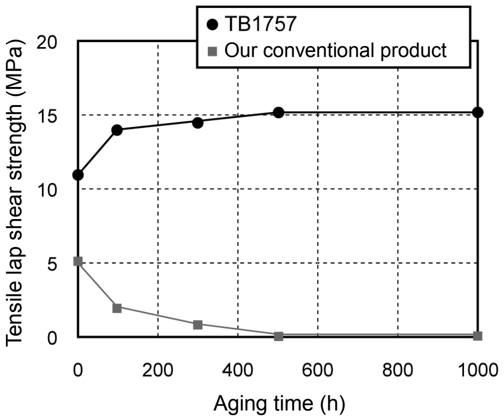

Figure 6. Heat resistance (bonding strength at 120°C after aging at 120°C)

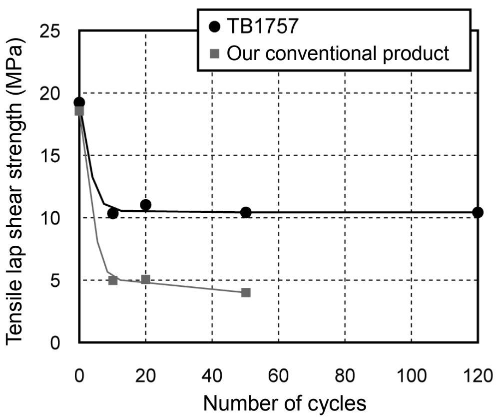

Figure 7. Thermal cycle resistance

Figures 5 and 6 indicate that TB1757 maintains excellent bonding performance even under high temperatures. In particular, TB1757 retains its initial bonding strength even after exposure to aging of 120°C x 1,000 hours and measurement under heated conditions. No conventional product to date has offered such exceptional and stable bonding performance.

Figure 7 shows that TB1757 also provides excellent thermal cycle resistance. Conventional instant adhesives generally provides poor thermal cycle resistance due to their hardness and brittleness after curing. In contrast, TB1757 maintains bonding strength exceeding 10 MPa after 100 cycles, a testament to its capacity to withstand rapid temperature changes.

Based on the above, we may conclude that water, humidity, heat, and thermal cycle resistance, widely considered poor with conventional instant adhesives as shown in Table 1, have been greatly improved in TB1757.

3-3 Applications for ThreeBond 1757

TB1757 applications cover a wide range of fields including wet and other conditions to require high reliability, which conventional instant adhesives could not support. Since TB1757 has not just high durability but ultra-fast curing properties, we expect it to help improve productivity on high-speed production lines. This indicates that TB1757 can replace epoxy resins and acrylic resins previously selected for their reliability despite the fact that they require furnaces or irradiation units, making it possible to significantly streamline production lines through a simple instant adhesive that cures at room temperatures and humidity.

Some major applications are as follows:

(1) Adhesion of parts for automobiles, air carriers, electric, electronic, and general applications that demand high water, humidity, and heat resistance
(2) Adhesion of weather-stripping in windows of automobiles, etc.
(3) Adhesion of rubber and elastomer parts in rubber gaskets, etc, which require high water and humidity resistance
(4) Adhesion of motor magnet parts
(5) Adhesion of parts for electronic installation

Conclusion

Over half a century has passed since instant adhesives entered practical use. During this time, numerous companies have marketed a wide range of products, with fast-curing one-part adhesives that adhere to a wide range of adherends, ensuring to use them in various applications and purposes. But instant adhesives also have disadvantages, including poor water and heat resistance, which have discouraged their adoption for applications requiring high reliability. We have undertaken the challenge of pursuing ultra-fast curing properties and delivering high reliability in the applications of instant adhesives to fully leverage their advantages. We believe that the two products introduced in this issue will help simplify the design for and enhance the efficiency of factory production lines. Such designs are expected to reduce the energy consumed upon production, as well as the total cost of production, while contributing to environmental conservation.

In closing, we appreciate your continued support as we strive to meet the needs of customers while pursuing efforts to develop new applications and open up new markets.

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