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Automobile Coating Agent

Introduction

Over the years ThreeBond has developed and marketed chemical products for automobile maintenance targeted to the automotive aftermarket. These products include brake cleaners for use in brake maintenance, chassis paints to serve as an anti-rust coating for automobile undercarriages, and anti-rust and lubricating agents for use in auto repair, inspection, and maintenance. Meanwhile, in recent years, the automobile industry has been faced with growing concern over the issue of global environmental conservation; consumers are demanding cars offering higher mileage, enhanced environmental friendliness, and increased safety. Furthermore, consumers are increasingly insisting on longevity, a lasting appearance, and comfort in the cars they purchase. In order to keep pace with such heightened environmental awareness and to respond to these changing consumer demands, ThreeBond has applied its expertise in a variety of resin and coating technologies accumulated over the years since its founding to develop a coating agent that will enhance both the interior and exterior of the automobile.

The present report will introduce a body/wheel coating agent which was placed on the market in 2005, a windshield water repellant, and a tire-coating agent, the latter two of which were introduced to the market this year, in addition to a discussion of the peripheral technologies associated with these products.

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1. Body/Wheel Antifouling Coating Agent

Admixtures of wax and petroleum solvents were traditionally marketed as polishing wax to add gloss to the auto body. Then, with the appearance of silicone compounds and fluorine compounds on the market, water repellency became recognized as an important feature of a product, in addition to gloss. However, as these products permeated the market, their adverse effects have come to attention—in particular, the presence of water spots, or marks arising from contact with water, raindrops, or the like.

Unlike conventional water-repellant coating agents, the polysilazane-based ThreeBond 6644 Series (Ultra Glass Coating) coating agent for automobiles actually prevents water spots and stains through its low water repellency.

1-1. Polysilazane

Polysilazane is a high polymer compound made of repeating units of silicon (Si) and nitrogen (N) in a molecular chain. The compound converts to silica (SiO_2) through oxidation reaction—a useful, high-tech, material property suitable for applications such as high-performance insulating coatings for electronic devices[1)] and functional transmissive coatings[2)].

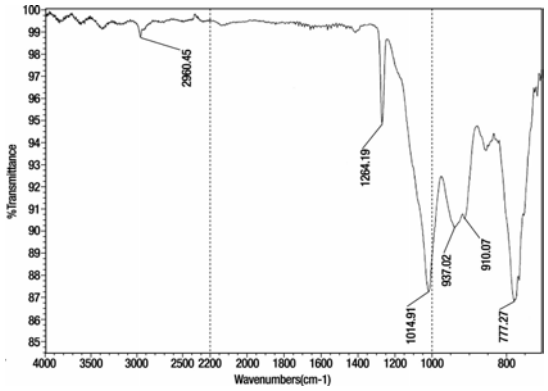
$$–(Si–N)n– \rightarrow – (Si–O)n–$$

In the ThreeBond 6644 (“Threebond” is hereinafter abbreviated as “TB”) series, polysilazane has been adopted as a base to produce a new type of automobile coating agent that in fact forms a glass (SiO_2) coat on the auto body.

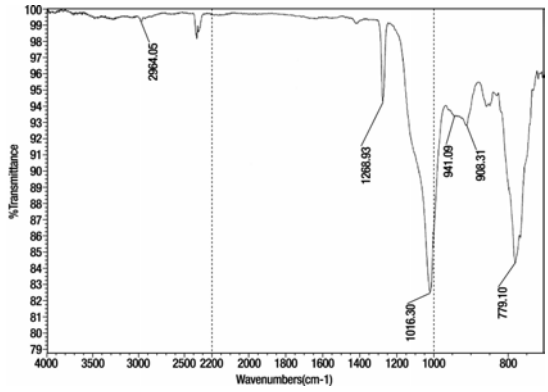
Figure 1 presents the infrared (IR) spectra obtained by infrared spectroscopy, which shows how the applied TB6644 auto-body coating agent and TB6644B curing accelerator is converted into a glass coating. As the figure shows, the intensity of the (Si–N) peak at 900-950 cm^{-1} decreases while that of the (Si–O) peak near 1,015 cm^{-1} increases relative to the ($Si–CH_3$) peaks near 1,265 cm^{-1} and 780 cm^{-1}, reflecting the conversion from Si–N to Si–O.

1-2. Low Water Repellency of the Glass Coating

Mainstream auto-body coating agents traditionally boasted high water repellency, with water droplets beading and bouncing off the vehicle body to which the agents were applied. However, recent years have witnessed a growing awareness of the problem of water-spot formation—e.g., marks from raindrops or other water marks caused by the beads of water remaining on the auto body. Since such water droplets are likely to contain the atmospheric pollutants nitrogen oxide (NOx) and sulfur oxide (SOx) that cause acid rain, the drying of such water droplets on the auto body often results in a residue of more strongly acidic droplets. Such residues corrode the paint and may cause so much damage as to require complete re-painting of the automobile.



Immediately after application



After curing

Figure 1. IR spectra of TB6644/6644B coating

These disadvantages of water-repellant agents have been overcome with the TB6644 series product, through the adoption of a strategy of low water repellence. Although the definition of hydrophilic characteristics and water repellency are rather ambiguous, generally, a surface of a solid is considered to be water repellant when the angle of contact with water is over 90 degrees, and when less than 30 degrees, is considered hydrophilic. The angle of contact for the TB6644 series is 75–80 degrees, and this property is what provides a surface that reduces residual water droplets compared to conventional water-repelling agents.

1-3. Anti-fouling Effect of TB6644

Photo 1 shows the results of a test performed to study the product's anti-fouling properties. An artificial dirt solution was prepared by creating a suspension of industrial test powder (JIS Z 8901) in ion-exchanged water with pH adjusted by sulfuric acid, followed by observation for evidence of the adherence of stains. It can be seen that the block treated with TB6644 coating (right) features less adhered staining than the untreated block (left).

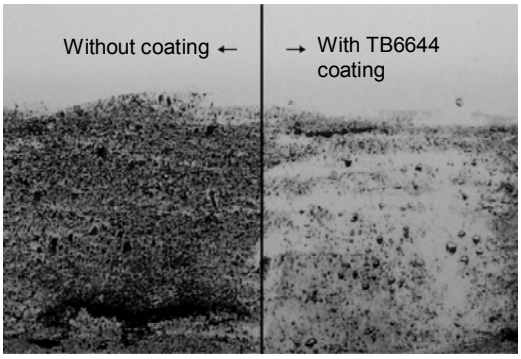


Photo 1. Results of stain prevention test using TB6644

1-4. Weather-resistance of TB6644

Figure 2 shows the results of an accelerated weathering test using TB6644.

A TB6644 coat was applied to a painted test steel plate and used as a specimen for an accelerated weathering test using a weathering machine. At all stages during the test, higher gloss is retained by the TB6644-treated surface relative to the untreated surface. The difference in the inclinations of the plotted lines indicates that the loss of glossiness may be slowed by nearly 25% through application of TB6644.

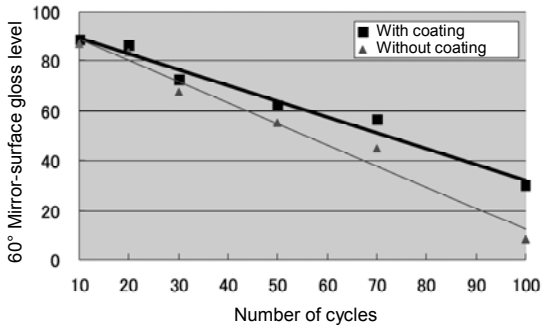
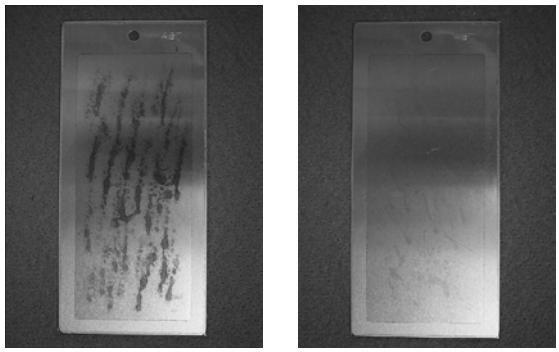


Figure 2. Results of weathering test using TB6644

1-5. Protection from Iron Powder with TB6644G

The TB6644G is an aerosol version of TB6644 designed for aluminum wheels. Applying TB6644G offers protection from staining for aluminum wheels.



Without TB6644G application | With TB6644G application

Photo 2. Protective effect of TB6644G against iron powder

Photo 2 shows the results of an iron-powder adhesion test using TB6644G. Significant degrees of discoloration are evident in the untreated aluminum test specimen (left) compared to the aluminum test specimen treated with TB6644G (right). This discoloration could neither be removed by cleansing agents nor physical cleaning using a cloth and was found to be the result of chemical deterioration (electrolytic corrosion). The results show that TB6644G is effective in preventing corrosion of the aluminum wheel due to adhesion of iron powder.

[Test method]

(1) A coat of TB6644G is applied to a test specimen.
(2) 0.5 grams of iron power was sprinkled onto each test specimen.
(3) Approximately 1.8 grams of ion-exchanged water was sprayed onto each test specimen.
(4) The test specimens were placed in a thermostatic oven set to 80°C for 30 minutes.
(5) The test specimens were removed from the oven and steps (3)-(4) (spraying of water and drying at 80°C) were repeated a total of 10 times.
(6) The test specimens were left to cool to room temperature, and the iron powder on the surface was removed using an air blower (approx. 0.2 MPa).

Some car owners want to drive shiny cars, others want to reduce the frequency at which they must wash them. But regardless of the various motives of drivers, car owners will always want to protect their beloved possessions from stains and deterioration. The TB6644 series (Ultra Glass Coating) is a coating agent that responds to these desires.

2. Windshield Water Repellant

Since 1992, a dramatic increase has been recorded in the volume of products shipped that add water-repellant properties to windshields for greater visibility in rainy conditions. Initially, solutions were rubbed onto the glass to form a hydrophobic coat on the windshield surface, but later, products that were combined with windshield washer fluids appeared, offering simultaneous application of the water repellant with the washer fluid.

In fiscal year 2005, water repellants for glass surfaces came in fourth place among top-grossing chemical products for automobiles, after two types of anti-freeze, three types of brake fluids, and windshield washer fluids.[3] Furthermore, as for the windshield washer fluids that ranked in third place, two types with water-repellant properties (with 'WC' classification) were added to the list of product types in the 2001 revision of JIS K 2398. Thus, the trend in the incorporation of water-repellant properties in windshields is not a passing fad—these products are now recognized as standard.

2-1. Water-repellence of Solid Surfaces

Liquids are retained at a certain angle (angle of contact) with the surface of a solid. The following relationship holds when γ_S is the surface tension of the solid, γ_L is the surface tension of the liquid, γ_{SL} is the interfacial tension between the solid and liquid, and θ is the angle of contact (Young's equation):

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos\theta$$

According to Young's equation, when the surface tension of the liquid is constant, $\cos\theta$ will decrease with decreasing surface tension of the solid γ_S, *i.e.*, the angle of contact will increase.

Since in practice it is difficult to measure the surface tension of the solid γ_S, Zisman proposed the use of the critical surface tension of solids (γ_C), which is determined by measuring the angle of contact for solids using liquids of known surface tension values and then by extrapolation to a zero angle of contact ($\cos\theta = 1$).

Table 1 lists the critical surface tension of some solids.[4]

Table 1. Surface structure and critical surface tension

Surface structure	γ_c (mN/m)
$-CF_3$	6
$-CF_2H$	15
$-CF_2-CF_2-$	18
$-CF_2-CH_2-$	25
$-CH_3$ (monolayer)	23 - 24
$-CH_2-CH_2-$	31
$-CCl_2-CH_2-$	40
$-C(NO_2)_3$ (monolayer)	42

The approach of "surface free energies," which is expressed in units of energy per unit surface area (J/m^2), is often adopted for studying surface wetting. On the other hand, the above surface tension is expressed in units of force acting on unit length (N/m), and since energy = force × distance (J = N·m), $J/m^2 = Nm/m^2 = N/m$, and so it may be seen that the surface free energy and surface tension are equivalent as physical quantities.

2-2. Application to Water Repellants for Automobile Windshields

From Table 1, it may be seen that the introduction of fluorine compounds on the surface results in low critical surface tension, and thereby enhances the water repellency of the surface (which equates to an increased angle of contact).

ThreeBond has taken advantage of this property and now proposes a water-repellant surface-treating agent for automobile windshields that contains silane compounds featuring a perfluoroalkyl group and organopolysiloxane.

Silane compounds having a perfluoroalkyl group react with a glass surface by the highly reactive functional group produced through hydrolysis, which results in the incorporation of the fluorine compound into the glass surface. This gives the glass surface high water-repellant properties (Figure 3).

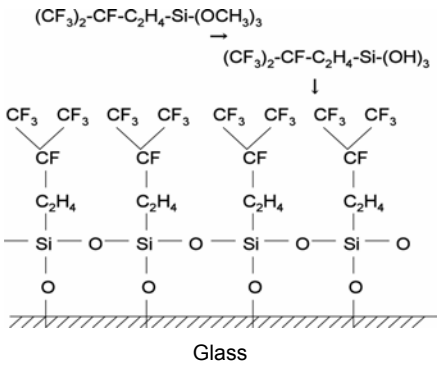


Figure 3. Schematic image of incorporation of a perfluoroalkyl silane compound onto a glass surface

The following section will introduce the TB6550E, a new glass water repellant for automobile windshields offering high water repellence and improved durability, now available from ThreeBond.

2-3. TB6550E — High-durability Water Repellant for Glass

Some water repellant products for automobiles require a process of mixing several fluids before application to obtain the necessary durability of the water-repellent effect. Product A by a rival company is just such a product, with a product package consisting of four types of solutions (a primer agent, water repellant fluid 1, water repellant fluid 2, and a post-treatment agent). After application of the primer agent, water repellant fluids 1 and 2 must be mixed prior to their application, and the special post-treatment agent must also be applied as a finishing coat. Thus, to obtain the desired water-repellent coat, all four solutions must be used.

On the other hand, only two solutions are required to apply TB6550E: a primer and the water repellant fluid. There is no need for measuring or mixing, and the process may be completed simply by wiping the coat with the dry towel included in the package.

Not only does the TB6550E-treated glass surface display an extremely large angle of contact of over 100 degrees, but also offers greater durability of effectiveness, lasting far longer that that of similar products from other companies.

Photo 3 shows photographs of water droplets on TB6550E-treated and non-treated glass surfaces* taken during measurement of the angle of contact.

Untreated glass surface
Angle of contact = 15°

Treated glass surface
Angle of contact = 114°

Photo 3. Water repellency of TB6550E-treated and untreated glass surface

* The water repellency (angle of contact) of the glass surface is subject to change depending on conditions such as adhesion of dirt.

Figure 4 is a graph showing the relationship between the number of polishes and angle of contact of the glass surfaces treated with TB6550E and competing products after polishing the surface with abrasive powder. It may be seen that the angle of contact for the TB6550E-treated glass surface is better retained compared to other products, and from the inclination of the plot, it may be concluded that the TB6550E coat lasts 2.5 times longer than other products.

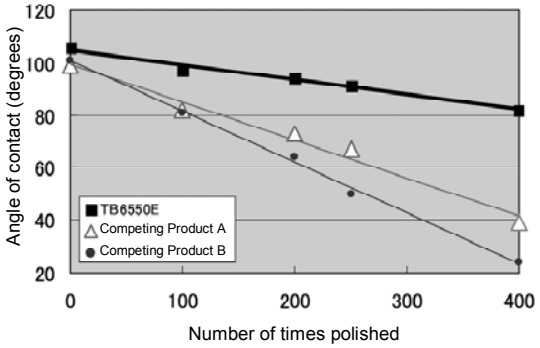


Figure 4. Durability of water repellency of TB6550E

2-4. Ice Suppression Effect of TB6550E

The ability of silicone resins and fluorine resins to resist the accretion of snow and ice have been studied extensively, with practical applications in the railway, communication, and energy fields.[6)]

In addition to greater visibility in rainy conditions—for a safer driving environment—the TB6550E also prevents or suppresses the accumulation of snow, ice, and frost on the windshield. It is our hope that this feature will contribute to the conservation of energy and ultimately to the preservation of the global environment by reducing the length of time people need to warm up their cars to remove snow, etc.

3. TB6641B Ultra Tire Coating Agent

The TB6641B is a protective coating agent for tires that forms a reactive resin coating on the tire surface. Unlike conventional silicone-oil type tire wax, which applies oil to the tire surface, TB6641B protects the tire from factors leading to degradation such as ultraviolet rays, allowing the tire to retain its original black color for longer.

3-1. Tire Weathering

Since tires are constantly subjected to excessive stress, one of the most important concerns naturally involves the weathering of the rubber tire itself. Some factors that promote weathering are:

(1) Oxygen and ozone in atmosphere

(2) UV radiation and direct sunlight

(3) Other factors (rainwater, oil, heat, etc.)

All of these factors affect the tires on a daily basis. Thus, the rubber compounds for tires always contain anti-aging agents that protect the tires from

such factors by suppressing the deterioration that occurs when the tires are subjected to these factors (referred to as the "main chain scission reaction") or by seeping out to the surface to form a coating. Since the anti-aging agents are brown, the tire surface will also feature a brownish discoloration (hereafter referred to as browning).

In the browned condition, tires will have some adverse characteristics, such as:

(1) appearing less attractive

(2) soiling hands or clothes when touched

The browning may be eliminated by washing the tire surface, but since the tires will continue to be subjected to the factors leading to degradation, they will ultimately turn brown again.

3-2. Anti-weathering Mechanism of TB6441B

Figure 5 shows how the anti-weathering mechanism of TB6641B works.

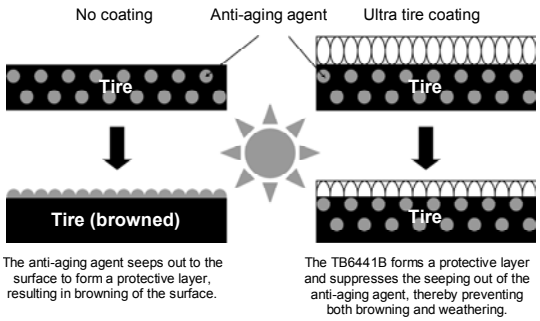


Figure 5. Mechanism of weathering prevention by TB6641B

Since TB6641B forms a protective coating for the tire in place of the anti-aging agents, the tires will remain free from browning and the tires will be protected while retaining their black color.

3-3. Durability of the TB6441B Coating

Table 2 presents the durability data for TB6641B and competing products.

Table 2. Comparison of coating durability data

	TB6641B	Competing Product A	Competing Product B	Competing Product C
	Water-based	Water-based	Oil-based	Oil-based
	Tyre coat	Tyre coat	Tyre coat	Tyre wax
Durability PR (distributed by manufacturer)	Retains black tire color for an extended period	Super durability	Over 40 days	90 days
Accelerated weathering test for 10 days	◎ Coating retained	◎ Coating retained	× Coating not retained	× Coating not retained
Observation in actual running conditions	◎ Retained after 6 months	× Not retained after 3 months	× Not retained after 2 months	× Not retained after 2 months
Flexural fatigue test 2.4 million cycles	◎ Coating retained	–	–	–

3-3-1. Durability Test (Accelerated Weathering Test)

An accelerated test to verify the durability of the TB6641B coat was performed using an accelerated weathering test machine (specifically, a "xenon-arc-lamp weathering tester;" JIS B 7754). TB6641B-treated and untreated areas were prepared on a test specimen, and the test specimen was left exposed under the xenon-arc-lamp weathering tester for a period of time before observing the difference in the weathering condition.

Based on a visual comparison with the results of actual outdoor exposure tests, 10-day exposure under the xenon-arc-lamp weathering tester was concluded to be approximately equivalent to a six-month period of exposure in actual outdoor conditions. Photo 4 presents the photographs of the test results.

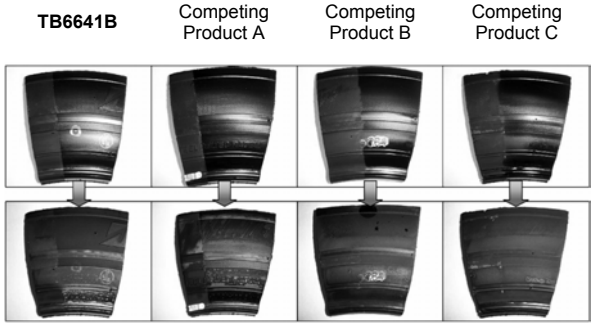


Photo 4. Tire surface after 10-day exposure under the xenon-arc-lamp weathering tester
(Top: before test; bottom: after test)

The results show that the coating remained on the tires with TB6641B and with Competing Product A.

3-3-2. Durability Test (Flexural Fatigue Test)

As a coating durability test in light of the actual running conditions of automobiles, evaluations were made using a flexural fatigue tester (or the

"De Mattia Flex Tester;" JIS K 6260). Photo 5 shows the tester in operation.

De Mattia flex tester　　Beam moves vertically to bend the test specimen

Photo 5. De Mattia flex tester

The flexibility fatigue test was repeated for 2.4 million cycles, assuming a travel distance per month of 4,000 km. As with the xenon-arc-lamp weathering tester, the test specimen was prepared assuming the following three cases.

(1) A new set of tires
→ Partially masked and coated

(2) A new set of tires with coating used for some time
→ Partially masked and coated, then exposed under the xenon-arc-lamp weathering tester for 10 days

(3) Used set of tires
→ The uncoated test specimen was exposed under the xenon-arc-lamp weathering tester for 10 days, then partially masked and coated.

The results of testing are shown in Photo 6.

Test specimen 1　Test specimen 2　Test specimen 3

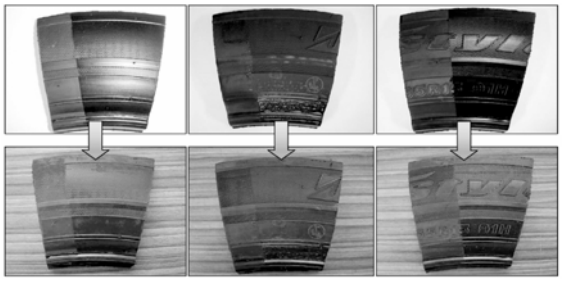


Photo 6. Surface of tire after testing with De Mattia flex tester
(Top: before test; bottom: after test)

The test confirmed that in all cases (Cases 1-3), coating was retained on the surface.

3-4. Plans for Future Development

The TB6641B allows tires to retain their blackness through the formation of a coat. However, to meet diversifying consumer demands, we must develop a tire coating that offers a "coated look," in addition to the "natural blackness" of the tire.

The demand for the "coated look" may be satisfied currently through the TB6640 and 6641 products, which contain silicone oil that leads to a gloss, as well as by the "tire wax" that has been on the market for some time. However, these products have low durability, and so the "coated look" does not last.

Figure 6 shows the difference in the mechanisms of the existing TB series products and the new one.

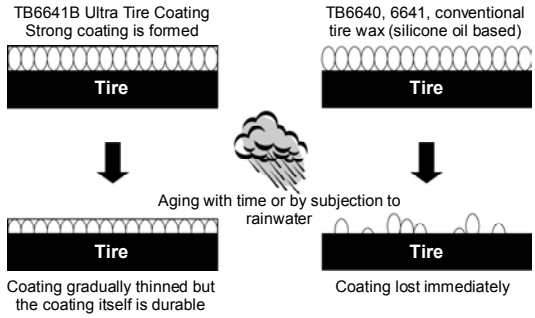


Figure 6. Comparison of weathering mechanisms to conventional TB products

Since TB6641B utilizes a special resin having membrane-forming properties, it can form a coating offering superior durability. Although the TB6640 and 6641 do not offer the same degree of durability, the silicone oil contained in these products allows them to offer a glossy look.

Figure 7 shows the correlation with existing TB products.

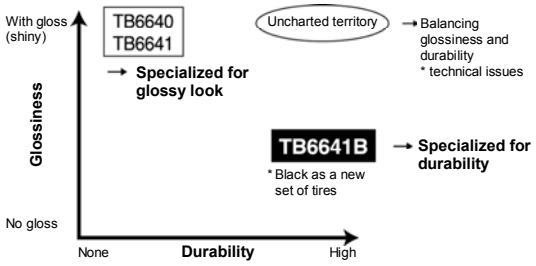


Figure 7. Correlation diagram of TB products

At present, ThreeBond is examining development strategies to produce a glossy yet highly durable coating based on the TB6641B, in the hopes of pioneering this promising uncharted territory.

4. Conclusion

The three products introduced in the present report are amenities that will enhance your driving experience. In recent years, media reports have suggested that new car sales have been in decline due to the development of public transportation networks, increasing car maintenance costs, changing lifestyles of the younger generation, and diversifying values. In response to these trends, car dealers (i.e., automobile retailers) are beginning to invent a variety of ancillary services to promote sales. To meet the market demands of these challenging times, ThreeBond has proposed and will continue to propose a lineup of chemical-product amenities that can be offered as services with new car purchases and that will encourage consumers to take advantage of automobile safety inspections and regular inspections. In the future as well, we will continue to place a high priority on the preservation of the global environment in our development of resin products and strive to meet market demands with our products.

References

1) Kozasa, T., et al.: Extended Abstracts of the 54th Spring Meeting of the Society of Applied Physics and Related Societies, 54(2), p. 868 (2007)
2) Iwamoto Y. et al.: J. Eur. Ceram. Soc., 25 (2/3), p. 257 (2005)
3) Japan Auto Chemical Industry Association: Report of Survey on Status of Japan Auto Chemical Industry for FY 2005 (2006)
4) W. A. Zisman: Ind. Eng. Chem., 55 (10), p. 19 (1963)
5) Patent # 2814259
6) For example, Saito, H. and Takazawa, H.: Journal of the Surface Finishing Society of Japan, 47 (7), p. 558 (1996)

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