

# Hitachi Chemical Technical Report

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**Hitachi Chemical**  
Working On Wonders



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(Top right)  
Plastic back door module



(Bottom right)  
High-strength resin gears



(Top left)  
Insulating varnishes



(Bottom left)  
Disc brake pads



Deputy Director  
Mobility Business Headquarters

Nori Imai


## Hitachi Chemical Products Contributing to Mobility Business

Hitachi Chemical began the manufacture of insulating varnishes for domestically made motors as a division of Hitachi, Ltd. in 1912. It broke away and became independent in 1962 with these varnishes as their original product. Subsequently, we expanded our business around electronic materials, and now provide optimal solutions to customers, centered on the four focus business areas of Information & Communication, Mobility, Environment and Energy, and Life Sciences.

The Mobility Business Headquarters was established in 2019. By adding two products (inorganic material products and resin products) to the five products (molded resin products, sheet-formed products, brake friction materials, powder metallurgy products, heat insulation components) handled by the Automotive Parts Division up to the previous fiscal year, sales accounted for over 30% of the sales of the Hitachi Chemical Group overall. As a result of this organizational change, the expanded material technologies for organic, inorganic, and metal materials were merged with design expertise for automobile parts to provide flexible solution proposals from a broader perspective. In the mobility field, the automobile industry is said to be undergoing a major, once-every-100 year revolution. By quickly grasping technical issues that differ from conventional ones, we can make proposals that lead to the creation of new value for our customers.

Electrification, Automation, and Connection are the driving forces behind the transformation of the automobile industry<sup>1) to 3)</sup>.

In comparison with internal combustion engines, Electrification delivers advantages including (1) low fuel cost, (2) no odor, noise or vibration, (3) low air pollution, and (4) CO<sub>2</sub> reduction effect. In particular, (3) and (4) are related to large cities and global warming, and their introduction has been accelerated by policy measures. Automation offers advantages such as (1) reduction of traffic accidents and (2) reduction of traffic jams. Driver error (recognition error, judgment error, operation error) is the major cause of traffic accidents, and there are high expectations of automation as a solution to this in our aging society. Congestion due to traffic capacity and driver behavior (such as deceleration) is also a major social problem in large cities. Automation such as the installation of ADAS (Advanced Driver Assistance System) is progressing in stages. Connection is partly related to Automation, such as car following. However, connecting the vehicle to a network outside the vehicle via a communication module changes the



“human-to-society interface” and how vehicles are used to give the capacity to provide various services. This is known as MaaS (Mobility as a Service), and it is said to present business opportunities in many industries besides transportation, including real estate, medicine, and events. In fact, new businesses are emerging one after another, such as car sharing; Uber, DiDi and other ride-hailing services; and collaboration with railways and local governments<sup>4)</sup>.

Technical issues and requirements related to progress in Electrification, Automation, and Connection are as follows: (1) weight savings (body, battery, motor, inverter, etc.), (2) bonding and joining of dissimilar materials, (3) control of sound and electromagnetic waves, (4) thermal management (heat storage, heat dissipation, etc.), (5) high battery capacity, (6) improved sensor and camera accuracy, and (7) processing large amounts of information. The Mobility Business Headquarters conducts research and development into these issues through close cooperation with customers and external research institutions. Examples include resin back doors to save weight, resin gears that combine silence and strength, and low dielectric constant, low VOC resin materials related to motors and inverters for electrification. In addition, with the aim of improving the speed of development and the accuracy of commercialization, we are also focusing on development process management, such as using a “virtual catalog” that introduces our ideas and technologies to promote dialog with customers from the concept stage.

The mobility business is a business that truly embodies Hitachi Chemical’s corporate vision of contributing to society through the development of superior technologies and products. I feel very fortunate to be able to be involved in this project during this period of change. Through technical innovation, we will continue to focus on reducing the environmental burden and improving the quality of life of each and every individual.

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# Automobile Related Products for Environmental Conservation and Energy Saving

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Environmental problems such as global warming and air pollution are becoming serious, and regulations on automobiles are increasing. Although the electrification of automobiles as an environmental countermeasure has been growing against the background of governmental preferences, internal combustion engines and hybrids are dominant for the time being. We are proactively developing auto parts and materials to realize environmental conservation and energy saving. This report refers to an overview of our R&D and manufacturing efforts on these issues.

## 1

## Introduction

The automobile industry is undergoing a once-in-100 year major reform with the shift to electric vehicles (EV). The factors promoting this reform include legal regulations and preferential treatment systems in response to environmental problems such as air pollution and global warming. Laws and regulations that obligate the introduction of environmentally-friendly vehicles, such as ZEV (Zero Emission Vehicle) regulations in California, USA; and NEV (New Energy Vehicle) regulations in China, directly drive the EV shift. Other standards, such as CO<sub>2</sub> and emission regulations, set criterion and indirectly promote the introduction of environmentally-friendly vehicles as a means to meet the target. Europe has the most stringent CO<sub>2</sub> regulations, and the 2021 criterion (95 g/km) requires a reduction of about 30% from the 2015 level. (The criteria in the US, Japan, and China are 113 g/km, 114 g/km, and 116 g/km, respectively.) These laws and regulations give preferential treatment to EV shift, and the rate of adoption of EV is predicted to be 8% in 2030 (1% in 2017)<sup>1) to 3)</sup>. However, the movement toward Life Cycle Assessment (LCA), which evaluates CO<sub>2</sub> emissions over the vehicle life cycle, has recently become active. If the method of measuring CO<sub>2</sub> emissions is changed to LCA, the CO<sub>2</sub> emissions of hybrid vehicles (HEV) become equivalent to or lower than those of EVs, depending on the technological progress. With the current regulations that target CO<sub>2</sub> emissions, EV is overwhelmingly superior, as CO<sub>2</sub> emissions when driving can be regarded as zero. In the case of LCA, however, EV CO<sub>2</sub> emissions are likely to exceed HEV when CO<sub>2</sub> emissions from power generation and battery production are added. The rate of adoption of EVs may fluctuate significantly depending on the situation, and we are closely monitoring trends<sup>4)</sup>. In this way, the environmental friendliness of automobiles is progressing in various forms, but some shared technologies are required for (1) energy saving, (2) electrification, and (3) air pollution reduction. In this report, we introduce our company's efforts to apply these technologies to automobile parts.

## 2

## Energy Savings

### 2.1 Weight reductions<sup>5)</sup>

To improve fuel efficiency with the aim of reducing CO<sub>2</sub> emissions, there are increasing demands for weight reductions, that are effective for any drivetrain. Reducing the weight by 100 kg is said to improve fuel efficiency by 1 km/L and reduce CO<sub>2</sub> emissions by 15 g/km. Methods to reduce weight are (1) moving to resins, (2) downsizing functional parts, and (3) thinner walls by using high-strength materials. Resins, of which CFRP (Carbon Fiber Reinforced Plastics) is a typical example, are lighter than steel and the other metals that are mainly used at present. In the automobile field, they are increasingly used for frames and structural parts and their use is expected to grow to the same scale as aircraft applications on a volume basis by 2030. Furthermore, due to their lightness and moldability, other plastics such as polypropylene and polycarbonate are being used for an increasingly wide range of automobile structural parts, electrical components, engine compartment parts, and fuel pumps. Hitachi Chemical products that are used include adhesives to connect components and parts, interior instrument panels and console boxes, exterior resin back doors<sup>6)</sup> and bumpers, resin gears in engine compartments, and housings for inverter power circuits as electronics system products. We are now working on developments to achieve further weight reductions in terms of materials and shapes. The resin back door uses polypropylene (PP), glass fiber (GF), and our adhesive to achieve weight reductions of 30%



or more compared to the conventional steel type. It uses 55% fewer parts, which improves productivity (Figure 1) (Figure 2). We are promoting the application of foam molding technology to various exterior parts to achieve further weight reductions in future. Resin gears also reduce the weight by 46% compared to steel gears and 58% weight reduction is achieved in the balancer system (Figure 3) (Figure 4). In the future, the company intends to expand their application by further increasing the strength.

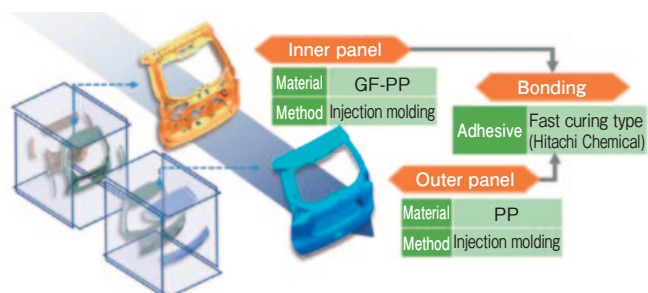


Figure 1 Structure of Back Door

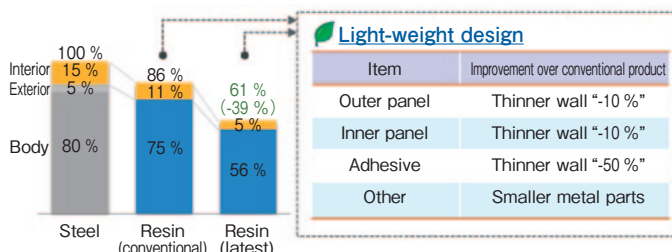


Figure 2 Weight Reduction Effect of Back Door Resinification

### Gears

	Steel gear	Resin gear
NO.1 gear	1.0 (steel)	0.2 (resin)
NO.2 gear	0.3 (steel)	0.1 (resin)
NO.3 gear	0.3 (steel)	0.1 (resin)
Total	1.3	0.6

46 % reduction



Figure 3 Weight Reduction Effect of Resin Gears

### Balancer system

Units	Steel	Resin
Number of journals	Qty 3	2
Journal diameter	mm OD29	OD23
Shaft length	Mm 265	185
Shaft mass	kgf 6.2	3.6

58 % reduction

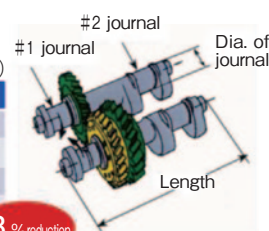


Figure 4 Weight Reduction Effect of Balancer System

## 2.2 Improving fuel consumption of internal combustion engines<sup>7)</sup>

Although the EV shift is predicted to continue until 2030, it is expected that approximately 90% of vehicles (mainly HEV) will have an engine, so that improving the fuel efficiency of internal combustion engines is an important development topic. Figure 5 shows the development trends to improve the fuel efficiency of internal combustion engine parts. Hitachi Chemical mass-produces high-strength gears through a combination of powder metallurgy and densification technology and mass-produces turbocharger parts<sup>8)</sup> with improved heat and wear resistance due to the precipitation of fine carbides. In the future, we intend to launch products that can improve fuel efficiency through weight reduction and downsizing.

	2015	2020	2025	Key technology
Trends in engine technology development		Lean burn		High strength (surface pressure resistance)
		Idle stop		Low friction
		Compact and lightweight		High strength
		Downsizing + turbo		Heat and wear resistance

Figure 5 Technical Road Map of Engine

## 3 Electrification<sup>9)</sup>

Electrification is an important technology that contributes to energy saving and the environment. The necessary functions are batteries, motors, and inverters. As products to support these functions, Hitachi Chemical mass-produces negative electrode materials<sup>10), 11)</sup> for lithium-ion batteries that have maintained top market share for more than 15 years based on high-capacity artificial graphite, high-power carbon-coated graphite, and high-capacity SiO; low VOC, high productivity impregnated varnish<sup>12)</sup> for motors; IPM (Intelligent Power Module) housings (Figure 6) using Al bus bars for inverters, and reactor cores that reduce core loss thanks to our original material technologies. Electrification is about to bring about significant technological innovations such as lighter batteries, and we intend to proceed with development work to establish the appropriate technologies.

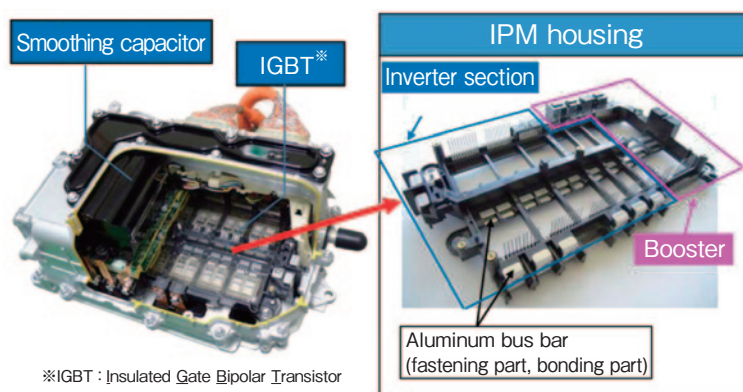


Figure 6 Structure of IPM System

## 4 Air Pollution Reduction

Air pollution is a problem that has a serious impact on the ecosystem, including harm to humans and the death of forests due to the release and movement of environmentally hazardous substances into the atmosphere. Environmentally hazardous substances include sulfur dioxide, nitrogen oxides, suspended particulate matter, carbon monoxide, hydrocarbons, and heavy metals, which need to be reduced or eliminated. We pioneered the industry by creating asbestos-free brake pads. Restrictions on the use of copper began in North America due to concerns that copper contained in the brake dust emitted from brake pads would contaminate rivers. Products sold in North America after 2025 are planned to be copper-free and their use will also be expanded overseas. We quantitatively investigated the effects of copper and achieved copper-free products by supplementing the functions with multiple metal and inorganic materials<sup>14)</sup>. In addition, we are focusing on eliminating solvent from the above-mentioned impregnation varnish, eliminating the use of heavy metals such as chromium, and mass-producing plated exterior sheets that do not require plating solution. In the future, we intend to proceed with developments to reduce and eliminate environmentally hazardous substances.

## 5 Conclusions

In this paper we introduced our environmental conservation and energy-saving initiatives. However, we are also actively expanding applications of light control film for heat management and RFIDs to improve the convenience of distribution. The automotive industry is undergoing further changes in car usage patterns known as “sharing” and is promoting autonomous driving and connected cars combined with electrification in a revolution known as CASE (Connected, Autonomous, Shared & Service, Electric). In particular, autonomous driving is achieved by linking many main technologies such as sensors, actuators, hardware, software, control, communication, image processing, and recognition. It is also necessary to link the automobile parts. Based on our core technologies, we will create new products that support CASE to make a contribution to society.

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# Primer-less Adhesive for Plastic back door Assembly

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## 1 Abstract

In recent years, automotive back doors made of plastic that are lightweight and have good designability have been making inroads. Primer-combined adhesive is superior in adhesion reliability, and has been applied to the assembly of the plastic back doors. However, it needs a primer application process, increasing the manufacturing costs of plastic back doors. In order to reduce the manufacturing cost, a primer-less adhesive is required, but achieving primer-less adhesion is difficult because plastic back doors consist mainly of Polypropylene (PP), which is a hard-to-bond material. We have adjusted the adhesive-substrates interaction and the physical properties of the adhesive, and then developed a new primer-less adhesive having good adhesion properties and adhesion reliability for PP-based plastics for back doors.

## 2 Characteristics of the Product

- Offers superior adhesion properties on hard-to-bond PP material, without using a primer.
- No drop in adhesion properties after long-term exposure to heat or hot water.

## 3 Background of the Development

Stricter regulations on CO<sub>2</sub> emissions due to the growth of the automobile market in recent years has led to increased demand for lighter vehicle bodies to lead to improved fuel economy. Against this background, Hitachi Chemical launched lightweight plastic back door modules<sup>1)</sup>. Polypropylene (hereinafter, “PP”) is the major component of plastic back door modules. PP has excellent mechanical properties but is generally a hard-to-bond material. For this reason, surface treatment and primer application were performed as pre-bonding treatments. **Figure 1** shows the adhesion process.

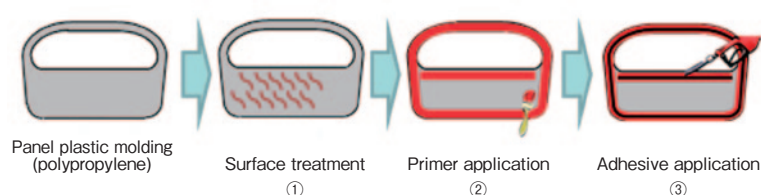


Figure 1 Adhesive process of Plastic back doors

It is known that eliminating the primer application process (**Figure 1** ②) leads to a significant cost reductions in the adhesion process. Therefore, we started to develop a primer-less adhesive but problems with adhesiveness and adhesion reliability still remained.



## 4 Technical Details

The newly developed product achieves primer-less adhesion through changes to the composition of conventional primer-combined adhesive. The details of the composition changes were determined from the results of surface analysis of the substrate and the results of various simulations. **Table 1** shows the values calculated by molecular simulations of the interaction energy between the two functional groups A and B in the adhesive and the substrate surface. **Figure 2** shows the stress simulation results of lap-shear model. Based on the results from **Table 1** and **Figure 2**, the interaction between the adhesive and substrate was increased and the stress concentration was reduced, making it possible to maintain the adhesive strength without using a primer.

Table 1 Interaction energy between functional group of adhesive and substrate

Functional groups in adhesive	Interaction energy (J/m <sup>2</sup> )
A	0.0874
B	0.1098

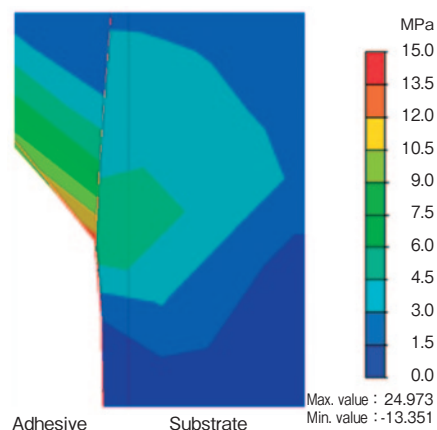


Figure 2 Stress simulation result of lap-shear model

**Table 2** shows the general properties of the developed product. This newly developed product requires no primer to achieve adhesion properties and adhesion reliability comparable to those of the primer-combined adhesive on plastic back door modules with PP as the major component.

Table 2 General properties of the new primer-less adhesive

Class	Item			Primer-combined adhesive	Primer-less adhesive (developed product)
Process properties	Primer			Yes	No
	Viscosity [Pa s]			1600	1600
	Two-part mixing ratio (base:hardener) [vol/vol]			1 : 1	1 : 1
	Curing time [min]			7.5	7.5
Adhesive properties	Manual peeling test	Initial	R.T.	CF100	CF100
	Lap shear test	Initial [MPa]	R.T.	3.5	2.4
				CF100	CF100
		Thermal aging [MPa]	90℃,336 h	3.3	3.6
		Warm water immersion [MPa]	40℃,336 h	CF100	CF100
				3.8	2.9
	CF100	CF100			
Tensile test	Elongation [%]		350	380	

\* CF100: 100% cohesive failure

## 5 Future Business Development

- Improvement of properties to expand substrate/surface treatment conditions

### 【References】

- 1) Teruhiko Iwata et al., : Plastic Back Door Module for Automotive, Hitachi Chemical Technical Report, 44, 21-24 (2005)

# Development of Low Dielectric Constant Polyamide-imide Varnish with High Breakdown Voltage

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## 1 Abstract

In recent years, industrial motors operating by PWM (pulse width modulation) inverter control have become mainstream. Surge voltages due to high-speed switching of the inverter (inverter surge) damage the coil insulation of the motors. To improve the coil insulation, reducing the dielectric constant of the enamel varnish is essential. For this purpose, a novel polymer alloy system with polyamide-imide and a reactive polymer has been developed. This varnish “HI-406P” exhibits a low dielectric constant and high breakdown voltage and is applicable to electric vehicle motor insulation.

## 2 Characteristics

HI-406P was able to improve the breakdown voltage from 12.1 kV to 15.2 kV by reducing the relative dielectric constant by 0.6 compared with the conventional product. The other properties of the enameled wire remain unchanged.

## 3 Background of the Development

Voltage and frequency have both become higher due to inverter control of industrial motors. Therefore, at the relative dielectric constant of conventional polyamide-imide varnish, it is difficult to suppress inverter surge that reduces the withstand voltage of motors. Polyamide-imide varnish using low dielectric materials has been developed as a method to suppress inverter surges. However, the drop in breakdown voltage and softening point due to thermal degradation or a hygroscopic environment are not satisfactory.

Therefore, Hitachi Chemical has developed a polyamide-imide varnish with excellent withstand voltage and heat-resistance characteristics by forming voids in the polyamide-imide varnish cured film and creating a fine phase separation structure of the reactive resin.

## 4 Technical Details

### 1. Development concept for HI-406P

Conventional techniques for lowering the dielectric constant suffer from problems of thermal degradation of the cured film and reduction in breakdown voltage due to moisture absorption by the cured film. To overcome these problems, we first created minute voids in the polyamide-imide cured film to reduce the dielectric constant, as shown in **Figure 1**. In addition, we adopted a reactive resin with a lower dielectric constant and different reactivity and polarity compared to the polyamide-imide resin. This formed a phase separation structure with a structural period of about 20 nm after curing, as shown in **Figure 2**. The dielectric constant was lowered with no reduction in other physical properties.

### 2. Breakdown voltage

The breakdown voltage was evaluated using the breakdown voltage of a twisted pair used as a winding. **Figures 3 and 4** show the breakdown voltage after the heat resistance test (260 °C/168 hours) and the moisture absorption test (60 °C/90 % R.H./24 hours). It achieved higher breakdown voltage compared to conventional polyamide-imide wire after both the heat resistance test and moisture absorption test.

The reduction of the relative dielectric constant could be cited as a factor for the improvement in breakdown voltage. But in addition, due to the adoption of a fine phase separation structure, the charged particles at the time of discharge wrap around the low dielectric constant voids in the reactive resin phase, and collide with the polyamide-imide phase. This gains some creepage

distance and reduces the collision energy of the charged particles due to reflection and scattering.

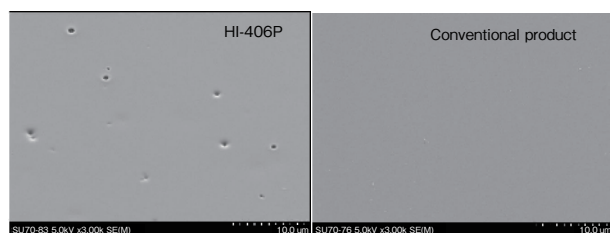


Figure 1 Comparison of SEM observation results between HI-406P film and conventional film

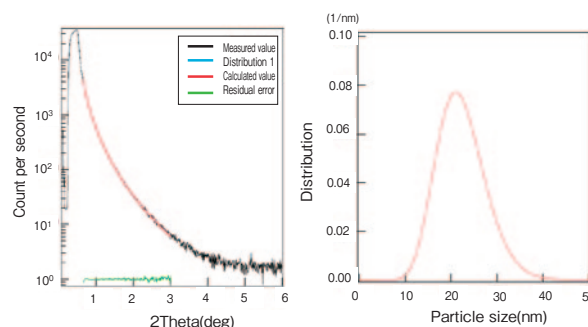


Figure 2 Small angle X-ray scattering results of HI-406P film

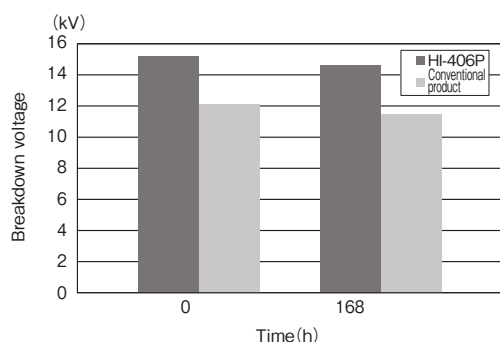


Figure 3 Comparison of breakdown voltage after heat resistance test between HI-406P and conventional PAI

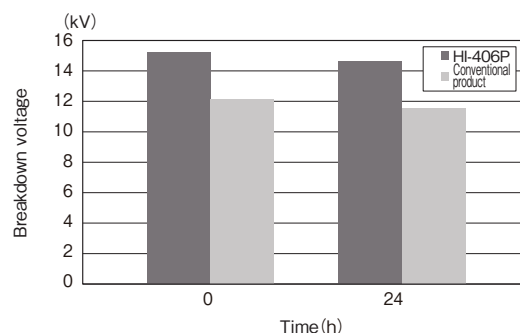


Figure 4 Comparison of breakdown voltage after moisture absorption test (60 °C / 90 % R.H.) between HI-406P and conventional PAI

### 3. General properties of HI-406P

Table 1 shows the general properties of HI-406P. HI-406P was able to improve the breakdown voltage from 12.1 kV to 15.2 kV by reducing the relative dielectric constant by 0.6 compared with the conventional product. The other properties of the enameled wire remain unchanged and we believe it can be applied in motors for electric vehicles for which demand is expected to grow rapidly.

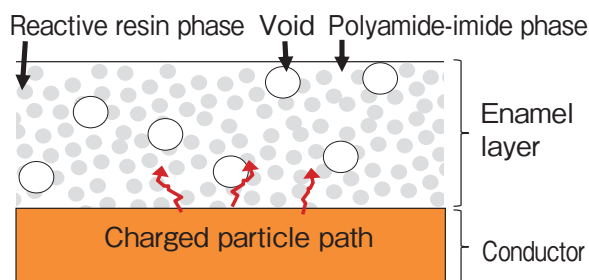


Figure 5 Schematic diagram of cross-section of enameled wire

Table 1 General1 properties of HI-406P

Item	Units	Conditions	HI-406P	Conventional product
Relative dielectric constant	-	1 kHz	4.0	4.6
Film thickness	mm	-	0.032	0.032
Enameled wire external appearance	-	Visual	Good	Good
Flexibility <sup>2)</sup>	-	20 % elongation	2d	2d
Adhesion <sup>2)</sup>	mm	Rapid extension method	2.0	2.0
Wear resistance <sup>3)</sup>	N	Unidirectional	17.3	16.8
Breakdown voltage <sup>4)</sup>	kV	Normal	15.2	12.1
Softening resistance <sup>5)</sup>	°C	Load: 0.7 kg	453	449
Glycerin pressure resistance	kV	Glycerin/saturated saline: 85/15	5.2	3.8

## 5 Future Business Development

- Further development of low dielectric constant technologies
- Development of insulation materials for next-generation electric vehicles

#### 【Related patents】

Patent No. 5896006 Patent No. 5804314 Patent No. 5880914

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# Copper-Free Brake Pads with Stable Friction Coefficient

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## 1 Abstract

Brake pads of automobiles are required to have a stable coefficient of friction, which is correlated to squealing and vibration that impair the quietness of the vehicle. Because of the increase in regenerative coordinated brakes and improved automatic control technology accompanying the spread of electric vehicles, friction coefficient stability is strongly demanded. On the other hand, due to concerns that the copper contained in wear powder discharged from brake pads contaminates rivers, restrictions on the use of copper began in North America, and products sold in North America after 2025 will be made copper-free. This article describes the friction coefficient stabilization of copper-free brake pads that started production in 2016.

## 2 Characteristics of the Product

- Meets 2025 North American copper regulations.
- Excellent quietness (superior squeal and judder characteristics).
- Good friction coefficient stability and low wear during high-temperature braking.

## 3 Background of the Development

The brake pad is a part that stops the vehicle by frictional forces. A thermosetting resin (mainly phenolic resin), metal fibers such as iron and copper, inorganic fibers, organic fibers, and friction modifiers such as abrasives and lubricants are mixed to form a friction material that is bonded to an iron plate (**Figure 1**)<sup>1)</sup>. Brake pads are required to have a high friction coefficient ( $\mu$ ), stability, wear resistance, and low abrasion of the brake disc. A stable friction coefficient ( $\mu$ ) leads to good braking performance and brake noise (**Figure 2**)<sup>2)</sup>. High abrasion of the brake disc leads to uneven disc wear which causes judder<sup>3)</sup>. Copper-free brake pads are being promoted in North America due to concerns about the contamination of river water by copper contained in brake dust<sup>4)</sup>. Copper offers high thermal conductivity, melting point, and ductility. It exists at the friction interface to affect the friction coefficient stability and the wear<sup>4)</sup>.



Figure 1 Copper-Free Brake Pads

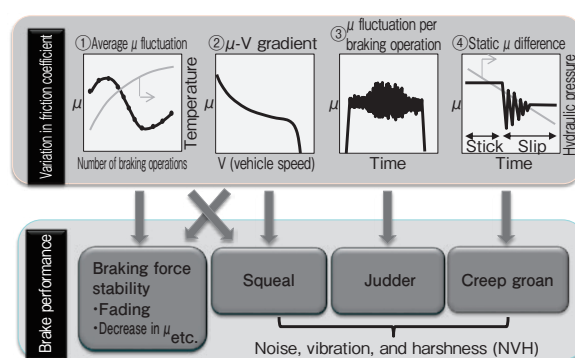


Figure 2 Relationship between Friction Variation and Brake Performance

## 4 Technical Details

Smeared copper can be seen on the friction surface of brake pads containing copper (**Figure 3**). Abrasiveness increased because the inorganic particles added to the friction material as an abrasive are retained in the copper film. With copper-free brake pads, the amount of disc wear is small even when the same amount of abrasive is added (**Figure 4**). Therefore, judder due to disc wear is unlikely to occur.

On the other hand, as the copper-free brake pad is in direct contact with the disc, changes in the organic matter contained in the brake pad are likely to appear as changes in the friction characteristics. The phenolic resin contained in the brake pad



is thermally decomposed by friction so that thermal decomposition products are generated on the friction surface. Therefore, friction coefficient ( $\mu$ ) becomes unstable near the resin decomposition temperature, and the high-temperature wear tends to increase. Catalysts such as metals are known to decompose the thermal decomposition products and contribute to stabilizing the frictional properties<sup>5)</sup>. In the copper-free brake pads we developed, potassium titanate was added that has a decomposition catalytic action on the decomposition products of phenolic resin<sup>6)</sup>.

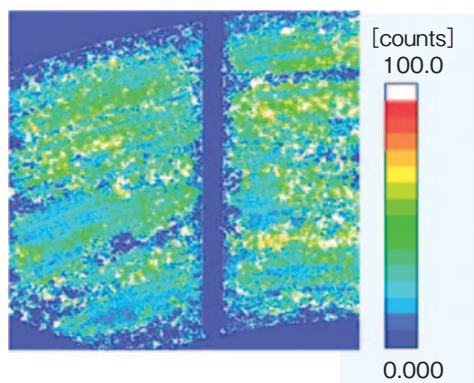


Figure 3 Copper on the Friction Surface of Copper-Containing Brake Pad

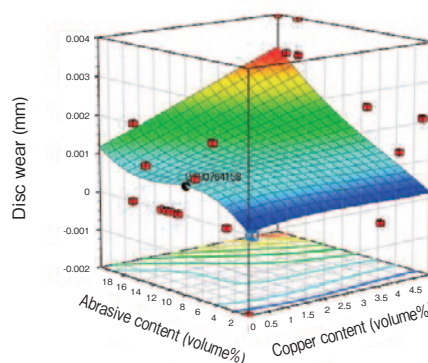


Figure 4 Effect of Copper on the Relationship between Abrasive Volume and Disc Wear

When friction tests are performed at different temperatures, the change in friction coefficient ( $\mu$ ) during braking increases near 400 °C even with copper-containing materials, and increased wear is apparent at higher temperatures (Figures 5 and 6). When titanate A is added, the increased change in friction coefficient ( $\mu$ ) and increased wear are observed at lower temperatures around 200 °C. However, when titanate B is added, the change in friction coefficient ( $\mu$ ) and increase in wear are only apparent at 500 °C.

The friction surface was observed when the change in friction coefficient ( $\mu$ ) was large. Unlike the friction surface when it was stable, the transfer film on the disk surface disappeared and the brake pad surface was pulverized into fine material. It is thought that the frictional interface fluidized due to the thermal decomposition products, making it easy for the friction material and the disc to come into direct contact and cause changes in the friction coefficient ( $\mu$ ) and increased wear.

The catalytic effect differed according to the type of titanate. In addition, the hardness and grain size also differed according to the type, and the average friction coefficient ( $\mu$ ) also differed. In the developed material, the mixing ratio was adjusted to meet the requirements for friction characteristics. This method also reduced brake noise.

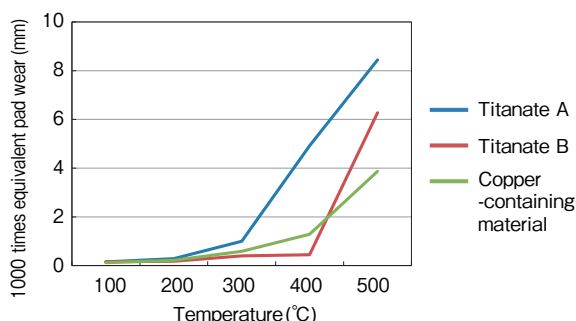


Figure 5 Temperature Dependence of Wear

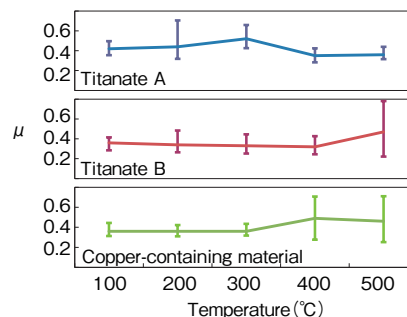


Figure 6 Friction Coefficient at Wear test  
(The Bar Indicates the Friction Coefficient Variation during One Braking)

## 5 Future Business Development

- Application expansion of copper-free brake pads
- Measures to meet requirements for self-driving technology and regenerative braking

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# Reactor Cores and 3D-shaped Motor Cores Manufactured by Powder Metallurgy

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## 1 Abstract

Powder Metallurgy has mainly been applied to structural parts in automobiles. We have developed and mass-produced magnetic parts manufactured by powder metallurgy. Recently, utilization of magnetic parts have been increasing due to the electrification of automobiles. In this report, we introduce reactor cores, which have low core-loss realized by our original lubricant, and 3D-shaped motor cores manufactured by powder metallurgy, which can downsize the volume of motors.

## 2 Characteristics

- Pure iron-based reactor core that suppresses core losses by applying Hitachi Chemical's original lubricant.
- 3D net-shaped motor core that exploits the features of powder metallurgy.

## 3 Background of the Development

Many magnetic parts have been industrially produced using powder metallurgy to date. The investigation and application of soft magnetic materials and parts manufactured by powder metallurgy have expanded in recent years, not only for home appliances and general industries but also for automobile parts. **Figure 1** shows a schematic of the operation frequencies and processes for sintered cores and soft magnetic composites. In the DC region, sintered cores have been used as various electrical components, such as yokes and plungers. In the AC region however, in recent years there has been an increase in applications of soft magnetic composites for use in high-frequency regions such as in motors and reactors. This may be due to the significantly improved magnetic properties of soft magnetic materials created by powder metallurgy. Generally, to manufacture soft magnetic composites, insulated iron powder is filled into a mold, compression molded, and heat treated. Conventionally, the molding pressure was low and only low-density soft magnetic composites could be created, so that the magnetic properties tended to be lower than those of melted materials. However, advances in manufacturing methods in recent years, such as high compression molding technology, high purity powder, and fine powder technology permit the manufacture of high-density soft magnetic parts with equivalent magnetic properties to molten steel. In addition, insulation treatment technology for the base powder surface has also evolved and can now be applied to motor cores and reactor cores used in AC magnetic fields.

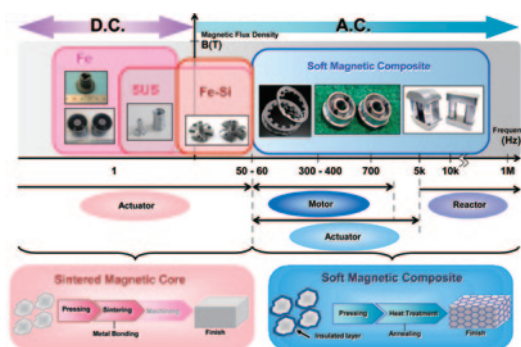


Figure 1 Schematic of the operation frequency and processes for sintered cores and soft magnetic composites

## 4 Technical Details

### Pure iron-based reactor core that uses original chemical lubricant

While it is easy to increase the density of pure iron-based soft magnetic composites, the metal powder itself is soft so that plastic flow that destroys the insulating coating is likely to occur at the sliding surfaces of the mold. The corresponding significant increase in eddy currents in the surface layer prevents the properties of pure iron being realized. The increase in eddy currents is fatal for magnetic components, such as reactors, that are driven in the high frequency range and this issue presented a serious barrier to the entry and expansion of pure iron soft magnetic composites into the reactor market. Consequently, Hitachi Chemical started the development of an insulating lubricant that can suppress the plastic flow in the surface layer and improve the insulation of sliding parts, with an aim to commercialize net-shaped products.

**Figure 2** shows the concept of the developed lubricant. The first aim was to suppress the plastic flow in the surface layer of

soft magnetic composites at the time of mold extraction. It was thought that plastic flow could be suppressed by applying a solid lubricant that can exist as a strong lubricating layer even at large extraction forces and can actively fill and remain in the voids to suppress plastic flow at the time of extraction from the mold.

To meet the second aim of maintaining and improving insulation, insulating oxide particles were dispersed in the lubricant as an additive. The fine particles selectively bind to the surface of the iron powder coating during molding and serve to protect the coating. In this way, we developed a new insulating lubricant for soft magnetic composites that functions both to prevent plastic flow due to the lubricant itself and to improve the insulation of the coating.

We have also developed inverter reactors for photovoltaic generation system using our original chemical lubricant. **Figure 3** shows a photograph of the external appearance of these products. These are soft magnetic composites for reactors that exploit the high inductance of pure iron and maintain low iron losses through methods devised for mold lubrication and insulation during molding. In the future, we will promote the development of reactors for automobiles in anticipation of xEV. **Figure 4** shows a photograph of the external appearance of a reactor core for automobiles. Currently, reactors for automobiles are equipped with a cut core of silicon steel sheets or a composite reactor core using Fe-Si alloy powder. It is anticipated that soft magnetic composites will be adopted as reactor core in the future to meet demands for higher inductance and smaller size.

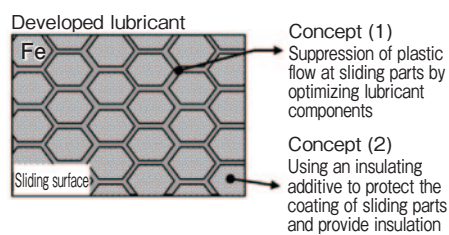


Figure 2 Concept of the developed lubricant

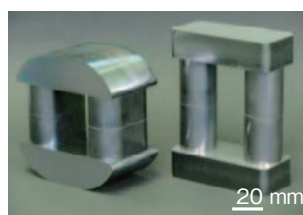


Figure 3 Inverter reactor cores for a photovoltaic generation system

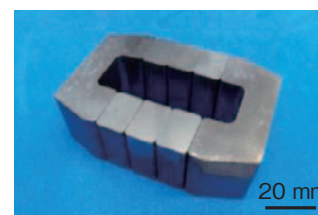


Figure 4 A reactor core for automobiles

### 3D net-shaped motor core

Soft magnetic materials currently used in the motor field are generally laminated electrical steel sheets. However, the laminates have a two-dimensional shape that makes it difficult to reduce the size of the motor when coil ends are included. On the other hand, a soft magnetic composite can be net shaped in three dimensions, and the motor core can be miniaturized by forming a three-dimensional magnetic circuit.

Hitachi Chemical has developed the EU-67 soft magnetic composite material with high magnetic flux density and low iron losses that exhibits excellent properties as a motor core. **Table 1** shows the magnetic properties of the EU-67 material. A comprehensive comparison of magnetic field analyses and actual machine evaluations indicated that claw pole motors that exploit the features of soft magnetic composites with a three-dimensional magnetic circuit, in particular, achieve the same improvement in output as 3-phase slotted motors of the same size using silicon steel plates. **Figure 5** shows the external appearance of claw-pole motor cores. When molding complicated shapes such as claw-pole motor core, multiple parts occur that have a small cross-sectional area in the press direction. This leads to concerns about problems such as failure of the mold when the necessary press force is applied. We were able to reduce the loads at positions of stress concentration and suppress damage to the mold by optimizing the mold shape by CAE analysis. The results of this investigation made it possible to perform molding with no damage to the mold even at a soft magnetic composite density of  $7.5 \text{ Mg/m}^3$ . **Figure 6** shows the results of CAE analysis.

In the case of axial gap motors too, it was possible to achieve the same improvement in output as a motor of the same size using silicon steel plates and the motor structure has a shape favorable for applying a soft magnetic composite core. **Figure 7** shows a photograph of a soft magnetic composite stator core and the structure of an axial gap motor. As can be seen from the external appearance, the coil ends in a radial gap motor protrude outwards on both sides, whereas in an axial gap motor, a permanent magnet rotor is arranged opposing the end surfaces of the soft magnetic composite stators. As the coil ends do not protrude, the motor can be made more compact.

Table 1 Magnetic properties of EU-67

Item	Property
Density	$7.5 \text{ Mg/m}^3$
Flux density : $B_{10000\text{A/m}}$	1.73 T
Iron loss : $W_{1T/400\text{Hz}}$	33 W/kg
Resistivity	$5000 \mu\Omega\cdot\text{cm}$



Figure 5 Claw-pole motor cores

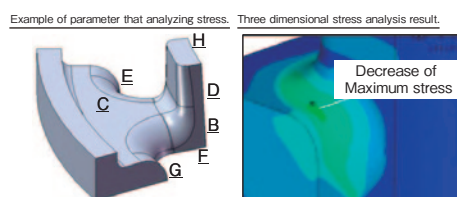


Figure 6 CAE analysis of a die

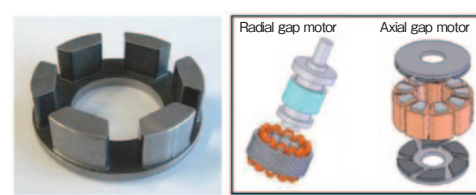


Figure 7 A soft magnetic composite stator core (left) and structure of an axial gap motor (right)

Thus, motors using a soft magnetic composite achieve the equivalent output to a conventional motor using silicon steel plates but with a significantly reduced motor volume. Due to their advantage of small size and thinness, these motors are expected to be adopted as xEV main motors and auxiliary motors in the future.

## 5 Future Business Development

- Development of pure iron-based reactor cores for automobiles
- Development of main and auxiliary narrow motors for automobiles



# Analysis of Water Consumption Mechanism of Lead Acid Batteries under Idling Stop System Operational Conditions

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## 1 Abstract

A vehicle equipped with idling stop system (ISS) has a function to stop its engine operation while stopping at traffic lights etc. A lead acid battery for an ISS vehicle is required to demonstrate a high charge acceptance for the improvement of fuel efficiency. Low water consumption (WC) is also required practically to eliminate the frequency of a water refill from a viewpoint of a maintenance-free battery. However, WC of a lead acid battery with a high charge acceptance tends to increase under the conventional over charge tests' conditions. In this report, WC behavior during a cycle test simulating ISS operational conditions (ISS cycles) is investigated by means of a real-time gas analysis. No simple correlation of a linear relationship appears between the two tests concerning the WC. No significant WC difference between high and low charge acceptance batteries was demonstrated under the ISS operational and these experimental conditions.

## 2 Characteristics of the New Technology

- Real-time analysis of gases generated due to water electrolysis during charging.
- Clarification of the mechanism of water consumption during the ISS cycle.

## 3 Background of the Development

ISS vehicles can improve fuel efficiency over existing gasoline vehicles with little change to the control system. Due to their excellent cost performance, global production is expected to continue to grow from now on. Many ISS vehicles are equipped with a function called regenerative charging that generates electricity from kinetic energy during deceleration and stores the energy in the battery. Charging is normally performed by consuming fuel to run a generator, whereas regenerative charging consumes no fuel to generate electricity and charge the battery. Therefore, the greater the charge acceptance and the larger the regenerative charging capacity, the more the fuel consumption can be reduced. For this reason, from the viewpoint of improving fuel efficiency, batteries for ISS vehicles need to have high charge acceptance. On the other hand, low water consumption is demanded from the standpoint of maintenance-free operation. But the same overcharge testing that has been being applied to lead acid batteries for conventional non ISS vehicles is still used as the method to evaluate the water consumption characteristics of the lead acid batteries for ISS vehicles. In general, lead acid batteries with high charge acceptance tend to show higher water consumption under overcharge testing conditions<sup>1), 2)</sup>, but sufficient knowledge has not been obtained about the water consumption behavior during the charge and discharge cycles for ISS.

## 4 Technical Details

Figure 1 shows the gas analysis equipment used in this study<sup>3)</sup>. The equipment consists of a hydrogen sensor, a gas flow sensor and an oxygen sensor. The water consumption behavior was analyzed by introducing the gases generated from the lead acid battery due to the electrolysis of water during the overcharge test and ISS cycle into the gas analysis equipment to analyze the gas generation behavior in real time. The test temperature was set to 60 °C in the assumption that the engine compartment where lead acid battery is located is hot. A total of 10 specifications of single-cell lead acid batteries with different charge acceptance were fabricated and evaluated for this test.

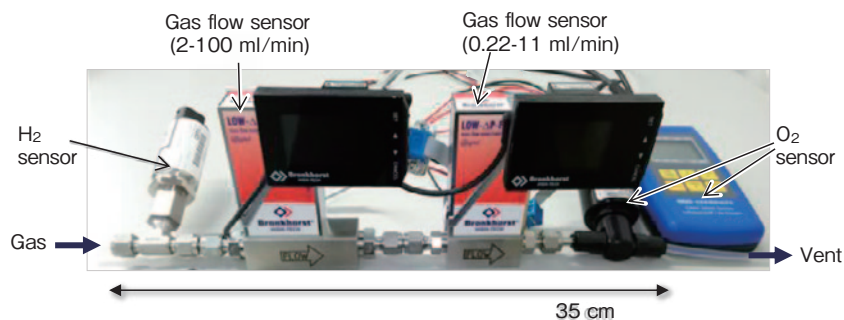


Figure 1 Gas analysis equipment

Figure 2 shows a comparison of the rates of water consumption during the overcharge test and the ISS cycle. The flow rates of gas generated during the test were used as an indicator of the water consumption rates. As shown on the horizontal axis, each water consumption rate during the overcharge test varied significantly according to the battery specifications. On the other hand, each water consumption rate during the ISS cycle did not show significant differences when the battery specifications changed, as shown on the vertical axis. This indicates that batteries that have a high water consumption rate in the overcharge testing that has been being applied to lead acid batteries for conventional non ISS vehicles will not necessarily have a similarly high rate of water consumption in the ISS usage environment<sup>4)</sup>. This difference is due to the fact that water electrolysis occurs as the main reaction in the overcharge test because the lead acid battery is fully charged, whereas the charging reaction of a lead acid battery occurs as the main reaction during the ISS cycle because the battery is not fully charged, and water electrolysis occurs as a side reaction<sup>5)</sup>. This suggests that a method of evaluating water consumption for lead acid batteries for ISS vehicles is required to replace the conventional water consumption evaluation tests.

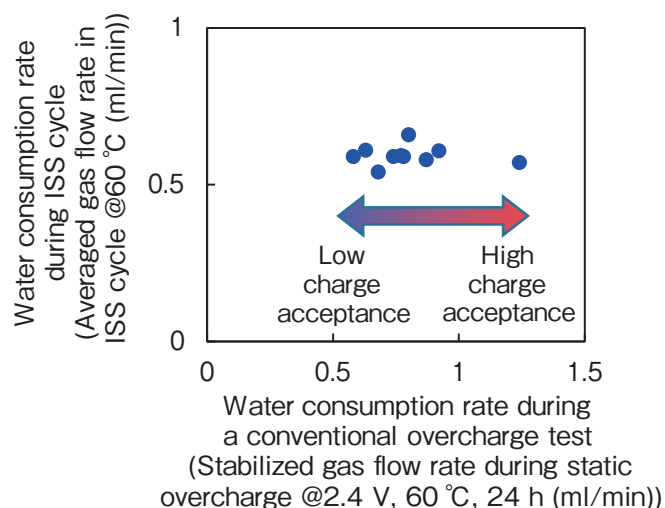


Figure 2 Comparison of water consumption rates during a conventional overcharge test and ISS cycle

## 5 Future Business Development

- Promoting standardization of new water consumption evaluation tests for lead acid batteries for ISS vehicles
- Application to improve the characteristics of lead acid batteries for ISS vehicles

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### 【Related patent】

Japanese unexamined patent 2019-79778 WO2019/082766

# Isotropic Conductive Film “IC-01A” for Low Temperature Connection and High Dimensional Stability

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## 1 Abstract

In recent years, smartphones and the like have become smaller, thinner, and multifunctional, and are mounted with various electronic components. Solder has been mainly used to connect these electrodes, but it is not suitable for members having low heat resistance. As an alternative to solder, our anisotropic conductive film can be connected at low temperatures and is effective even when there is an oxide film on the electrode surface. However, the dimensional stability after connection is low. Therefore, “IC-01A”, an isotropic conductive film that can be connected to an electrode having an oxide film and having high dimensional stability, was developed by combining conductive particles having a specific shape with an anisotropic conductive film and an adhesive composition that suppresses bleeding before and after connection.

## 2 Characteristics of the Product

- Applicable to a wide range of metal electrodes (gold, aluminum, copper, stainless steel, etc.)
- Can connect at 100 °C.
- High dimensional stability before and after connection.

## 3 Background of the Development

Devices such as smartphones incorporate many electronic circuits, and noise caused by electromagnetic waves emitted from the circuits causes deterioration in quality. Shielding the source of the electromagnetic waves and improved grounding of the circuit are effective countermeasures to this problem.

We received a request from an electronic component manufacturer to develop a new conductive connection film that can connect the metal foil of electromagnetic shielding parts to non-heat-resistant parts. Two properties are required: low-temperature and low-pressure connection to electrodes with an oxide film such as aluminum or copper, and high dimensional stability before and after connection. Hitachi Chemical has developed the world's first circuit connection material, ANISOLM<sup>®</sup> anisotropic conductive film. It is employed mainly in the field of flat panel displays<sup>1)</sup> and is more effective than solder for components with low heat resistance<sup>2)</sup>. However, pressure is required to flatten the conductive particles onto electrodes with an oxide film, and it suffers from issues of low dimensional stability due to the adhesive oozing out. We therefore started development to achieve both connection to electrodes with an oxide film and high dimensional stability based on the concept that stable conduction is possible without flattening the conductive particles.

## 4 Technical Details

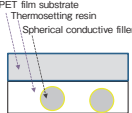
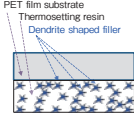
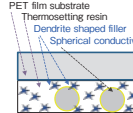
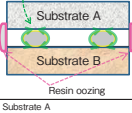
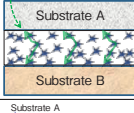
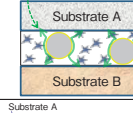
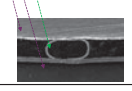
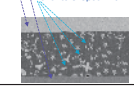
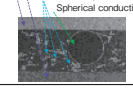
The development goal was to be able to connect to electrodes with an oxide film on the surface layer without flattening the conductive particles, that is, a low-pressure connection.

Based on the idea that it might be effective to break through the oxide film on the metal electrodes through local pressure application by the conductive particles, we first investigated various conductive particles, focusing on the particle shape, and selected dendritic metal particles with a sharp shape (hereinafter, “dendritic particles”). Next, we evaluated investigation item (1) that optimized the ratio of the high molecular weight component to reactive component to suppress the flow of the adhesive. As a result, it satisfied the standard value of the connection resistance immediately after connection (0.1 Ω or less) and the standard value for oozing of the adhesive (5 % or less). On the other hand, it significantly exceeded the standard values after the thermal

shock test. This seems to occur because, even if the flow of the adhesive is small at the time of connection and the dendritic particles are stacked and make contact with the electrode to ensure conduction, it is assumed that the dendritic particles could no longer contact the electrode due to shrinkage of the adhesive in the thermal shock test.

To solve this problem, plastic spherical conductive particles (hereinafter, "spherical conductive particles") plated with metal are used that enter between the dendritic particles stacked between the electrodes. As the spherical conductive particles have plastic cores with a linear thermal expansion coefficient close to that of the adhesive, these particles closely follow the expansion and contraction of the adhesive during the thermal shock test. It is thought that this makes it easy to maintain the contact of the dendritic particles with the electrode. Evaluation of investigation item (2) (product name: "IC-01A") that uses both of the two types of conductive particles above together shows that it suppressed the increase in connection resistance after the thermal shock test and met the standard values. Investigation item (2) achieved high contact reliability for contact with aluminum or copper, even at low contact pressure that did not flatten the spherical conductive particles. **Table 1** shows a comparison of various anisotropic conductive films. **Table 2** shows the general characteristics of "IC-01A".

Table 1 Comparison of Various Anisotropic Conductive Film

Item	Anisotropic conductive film (ACF)	Investigation item(1)	Investigation item(2) Isotropic conductive film IC-01A
Product structure (cross-sectional schematic)			
Diagram of connection state and current flow			
Cross-section example of connection part			
Typical required bonding pressure	1.0 MPa	0.2 MPa	0.2 MPa
Connection resistance*1 (Initial)	0.2 Ω	≤0.1 Ω	≤0.1 Ω
Connection resistance*1 (500cycles)	≤0.5 Ω	≤10 Ω	≤0.1 Ω
Adhesive flow ratio*2	36%	≤5%	≤5%

- \*1 Connection film size : 3 mm × 3 mm  
Substrate : 3 mm × 40 mm Al foil (25 μm<sup>2</sup>), 3 mm × 40 mm Cu foil (25 μm<sup>2</sup>)  
Bonding conditions : 120 °C / 10 s / 0.2 MPa  
RA test condition : Thermal cycle test 500 cycles (1 cycle : -40 °C / 30 min to 100 °C / 30 min)
- \*2 Connection film size : 2 mm × 2 mm  
Substrate : 18 mm × 18 mm slide glass (1.0 mm<sup>2</sup>) (Set connection film between two glass slides)  
Bonding conditions : 120 °C / 10 s / 0.2 MPa  
Adhesive flow ratio = (Connection film size (after bonding) / Connection film size (before bonding)) × 100

Table 2 General Characteristics of IC-01A

Item	Unit	Character
Resin type	-	Thermosetting
Thickness	μm	25
Base film	-	PET
Bonding condition	Temperature	°C
	Time	s
	Pressure	MPa
Connection resistance*1	Ω	≤0.1
Adhesive flow ratio*2	%	≤5
Peeling strength*3	N/cm	≥10
Elastic modulus(25 °C)	GPa	2.3

- \*1 Connection film size : 3 mm × 3 mm  
Substrate : 3 mm × 40 mm Al foil (25 μm<sup>2</sup>), 3 mm × 40 mm Cu foil (25 μm<sup>2</sup>)  
Bonding conditions : 120 °C / 10 s / 0.2 MPa  
RA test condition : Thermal cycle test 500 cycles (1 cycle : -40 °C / 30 min to 100 °C / 30 min)
- \*2 Connection film size : 2 mm × 2 mm  
Substrate : 18 mm × 18 mm slide glass (1.0 mm<sup>2</sup>) (Set connection film between two glass slides)  
Bonding conditions : 120 °C / 10 s / 0.2 MPa  
Adhesive flow ratio = (Connection film size (after bonding) / Connection film size (before bonding)) × 100
- \*3 Connection film size : 1.5 mm × 40 mm  
Substrate : 15 mm × 40 mm Al foil (25 μm<sup>2</sup>), 15 mm × 40 mm Cu foil (25 μm<sup>2</sup>)  
Bonding conditions : 120 °C / 10 s / 0.2 MPa  
Peeling angle : 90°

## 5 Future Business Development

- Searching for new fields of application
- Connection to curved parts

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# New Low Transmission Loss & Halogen-Free Multi-Layer Material “MCL-LW-990G”

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Information and Communication Business Headquarters

## 1 Abstract

The network devices for the next generation of wireless networks, called “5G”, need to use higher frequency for bigger data and higher speed communication. At higher frequency, the reduction of transmission loss on printed wiring boards (PWB) is essential to secure signal integrity. In response to such a situation, Hitachi Chemical has developed a new low transmission loss & halogen-free multi-layer material, the “MCL-LW-990G” series, which has lower transmission loss than conventional materials. “MCL-LW-990G (DZ)” can reduce transmission loss by about 21 % compared with “MCL-LW-910G”, has high reliability, and is promising for the next-generation high-speed and high-frequency communication devices.

## 2 Characteristics of the Product

- Excellent dielectric properties (dielectric constant, dissipation factor).
- Excellent transmission properties (low transmission losses).
- Excellent heat resistance and insulation reliability.
- Halogen-free multi-layer material.

## 3 Background of the Development

The 5th generation mobile communication standard (5G) is in partial commercial operation. It requires higher communication speeds and increased communication capacity compared to conventional technologies. In order to realize such high-capacity and high-speed communications, it is necessary to increase the signal frequency. Technological development is progressing, including network devices such as mobile phones, base stations, and data center servers that use the frequency band from quasi-microwave to millimeter wave. For printed wiring board materials used in such network devices, there are increasing demands to suppress signal degradation due to transmission losses on the printed wiring board.

Against this background, we have developed a new low transmission loss and halogen-free multi-layer material, the “MCL-LW-990G” series, to further reduce transmission losses.

## 4 Technical Details

### 1. Development concept for “MCL-LW-990G”

Transmission losses can be broadly divided into losses due to insulation layers (dielectric loss) and losses due to circuits using copper foil, such as conductor circuits and wiring boards (conductor loss). Dielectric loss can be reduced by using a low-polarity resin, but the adhesion to the conductor, heat resistance, and flame retardance are often inadequate. Therefore, Hitachi Chemical tried to achieve both properties by adopting a polymer blend using a proprietary denaturation technology that involves a co-crosslinking reaction with a high-polarity resin that is excellent in these properties. As a result, low-roughness copper foil that is effective in reducing conductor losses can be applied to reduce both the dielectric and conductor transmission losses.

### 2. General properties of “MCL-LW-990G”

Table 1 shows the general properties of the developed “MCL-LW-990G”. For purposes of comparison, the properties of a previous Hitachi Chemical material, “MCL-LW-910G”, are also shown in this table. The new materials have a dielectric constant (Dk) of 3.0 and a dissipation factor (Df) of 0.0017 at a frequency of 10 GHz. It has superior dielectric properties to our previous

material. In addition, CTE, Tg, and solder heat resistance are equivalent or superior to “MCL-LW-910G”, and the reliability can be seen to be excellent.

Table 1 General Properties of MCL-LW-990G

Items	Condition	Unit	LW-990G(D)	LW-990G(DZ)	LW-910G
Glass type	-	-	Low Dk glass	Lower Dk glass	Low Dk glass
Dk*	10 GHz	-	3.06	3.00	3.22
Df*	10 GHz	-	0.0020	0.0017	0.0033
CTE	TMA(Expansion)	ppm/°C	15	15	18
Tg	TMA	°C	200	200	200
Solder heat resistance	288 °C Float	s	> 300	> 300	> 300
Peel strength	HVLP 18 μm	kN/m	0.6	0.6	0.6

\*Cavity resonator perturbation method

### 3. Evaluation of “MCL-LW-990G (DZ)” transmission properties

The transmission characteristics (transmission losses) in the “MCL-LW-990G (DZ)” strip-line were evaluated. **Figure 1** shows the structure and specifications of the transmission loss measurement board, and **Figure 2** shows the transmission loss evaluation results. Compared with our previous “MCL-LW-910G” material, transmission losses at 40 GHz were reduced by about 21 % and excellent transmission properties were achieved even in the millimeter wave band.

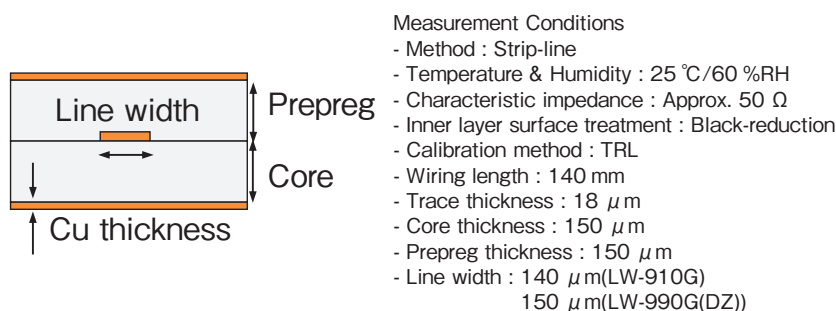


Figure 1 Structure of Transmission Loss Measurement Board

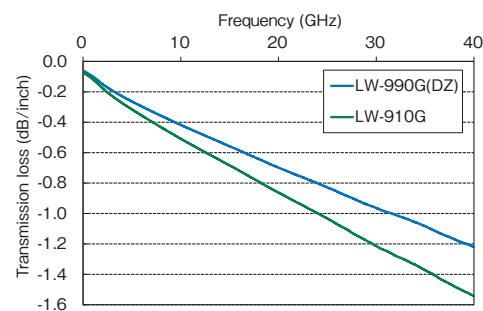


Figure 2 Transmission Loss Evaluation Results

### 4. Evaluation of “MCL-LW-990G” insulation reliability

Conductive anodic filaments (CAF) were evaluated between the through holes (hereinafter, “TH”). **Figure 3** shows the structure and specifications of the measurement board, and **Figure 4** shows the CAF evaluation results. The insulation properties of the “MCL-LW-990G (D)” and “MCL-LW-990G (DZ)” are good, with no drop in insulation resistance value from the beginning to 1,000 hours.

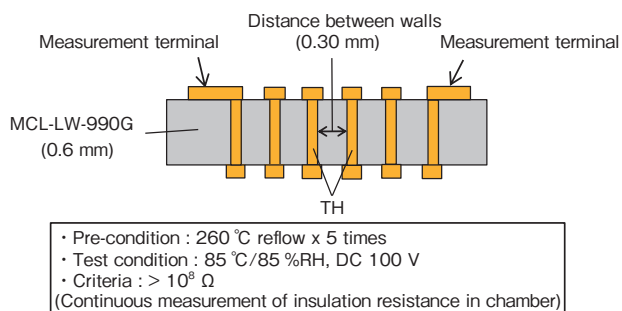


Figure 3 Structure of Insulation Evaluation Board

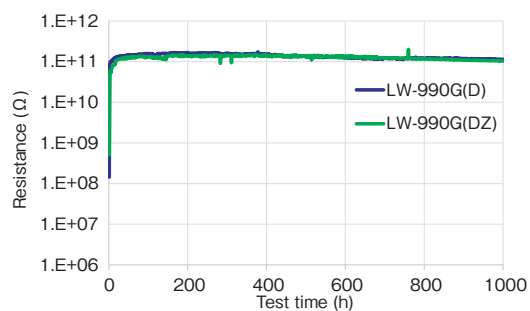


Figure 4 Insulation Evaluation Results

## 5 Future Business Development

- Development of new low transmission loss materials that can support the high-speed and large-capacity communications for next-generation network devices

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# Low-Melting Vanadate Glass

## Vaneetect Series VS-1298M

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### 1 Abstract

Recently, housing thermal insulation regulations have been promoted, and Vacuum Insulation Glass (VIG) has attracted attention for heat insulation applications for windows. Low-melting Glass is used for VIG to achieve high airtightness and high reliability.

We have developed Low-melting Vanadate Glass, “VaneetectII” (400 °C bonding) and “VaneetectIII” (300 °C bonding). However, II has a high bonding temperature, and III is expensive because it contains silver. Therefore, we have developed “VS-1298M” (350 °C bonding), a silver-free vanadate glass with an extremely low melting point.

### 2 Characteristics of the Product

- Lowest melting point (350 °C) with no silver content.
- Sealing is possible in the atmosphere, inert gas, or vacuum.
- Good bonding with glass, ceramics, or metals.

### 3 Background of the Development

Currently, lead/bismuth glass that seals at 450 °C is the mainstream of Vacuum Insulation Glass (VIG), but there are always demands for lead-free glass that melts at a lower temperature. The addition of silver is effective for lowering the melting point of vanadate glass, but silver is expensive. Therefore, our goal was to develop glass that bonds at 350 °C without using silver. The issues to be overcome and our development guidelines are shown below.

- (1) No silver content. As silver is assumed to be incorporated into the glass in a cation state. We studied with alkali metals which are cations, instead of silver.
- (2) Glass temperature characteristics: Softening point is about 310 to 330 °C, and bonding is possible at  $350 \pm 10^{\circ}\text{C}$ .
- (3) Crystallization temperature: Bonding temperature + 50 °C or above (400 °C or above). A high crystallization temperature is better, as low-melting glass loses adhesiveness when it crystallizes.
- (4) Coefficient of thermal expansion (CTE): Adjustable. If the CTE of the low-melting glass differs from the CTE of the adherend, the reliability is reduced due to peeling or cracking.
- (5) Chemical reliability: HAST, acid-, alkali-immersion tests and airtightness shall be equivalent to lead glass or bismuth glass.

## 4 Technical Details

Hitachi Chemical developed “VP-1298M” low-melting glass. The developed product contains no silver and can be melted and bonded at 350 °C. The glass transition temperature  $T_g$ , softening point  $T_s$ , and crystallization temperature  $T_{cry}$  were measured by differential thermal analysis (DTA). **Table 1** shows the measurement results for the newly developed product and a conventional product that bonds at 400 °C. In addition, we performed button flow test (hold at target temperature for 30 minutes) on compressed pellets of glass powder. The test results are shown in **Figure 1**. The pellet started to soften at 320 °C and flowed at 350 °C.

Table 1 Temperature Characteristics of Low Melting Glass

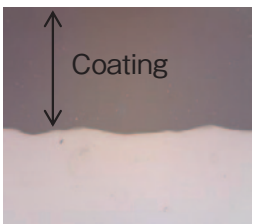
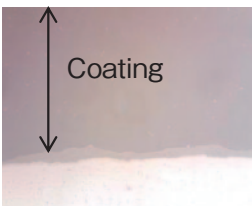
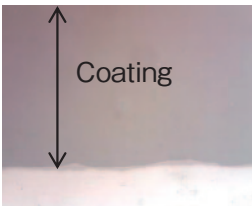
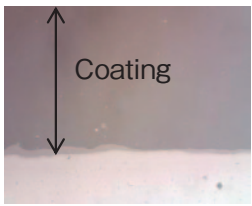
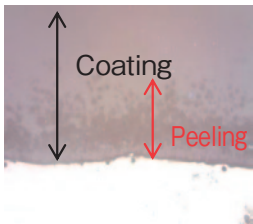
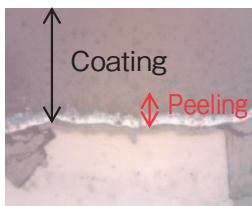
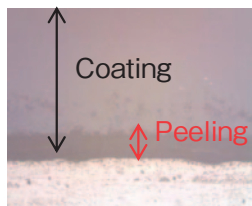
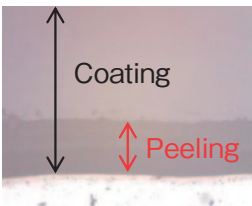
Sample		Developed product	Product that bonds at 400 °C
$T_g$	°C	261	312
$T_s$	°C	321	381
$T_{cry}$	°C	439	483



Figure 1 Button Flow Test of Glass Powder

The developed glass powder can be made into a paste by mixed with a thermal expansion filler, an organic solvent and binder resin. The glass paste can be applied in any place with a dispenser. We have developed “VS-1298M”, which has the same coefficient of thermal expansion as soda lime glass. Two soda lime glass (thickness 3 mm) were bonded at 350 °C with a bonding distance of 200  $\mu\text{m}$  using “VS-1298M”. And HAST, saline immersion, acid immersion and alkali immersion tests were performed. The results are shown in **Table 2**. “VS-1298M” is a little peeled off in the reliability tests, it has good chemical reliability.

Table 2 Reliability Test Result of VS-1298M

Test	HAST	Saline immersion	Acid immersion	Alkali immersion
Conditions	120 °C, 0.199 MPa, 48 h	100 g/L NaCl, 35 °C, 1000 h	0.25 mol/L $\text{H}_2\text{SO}_4$ , 50 °C, 2 h	0.5 mol/L NaOH, 50 °C, 2 h
Before test				
After test				

## 5 Future Business Development

- Provision of samples of the developed product and evaluation of their practicality



# High Toughness Liquid Crystalline Epoxy Resin

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## 1 Abstract

In recent years, increased fuel efficiency of moving vehicles has been demanded for the purpose of reducing the environmental burden, and resin composites are receiving attention as the lightweight and high-strength materials. However, resin composites are brittle compared with conventional metal materials, and so increased resin material toughness is required to address this issue. We have developed high-toughness liquid crystalline epoxy resins which can form higher order structures due to reaction-induced phase transitions in the cured materials. The resins show excellent handling properties in an uncured state, and the cured resins exhibit fracture toughness 3 times greater than that of general-purpose epoxies as well as high heat resistance properties due to the formation of crosslinking structures. Therefore, the resins are suitable as matrix resins for high-strength composite materials.

## 2 Characteristics of the Product

- Crystallinity controlled by modification of a mesogenic epoxy resin to permit solvent-free coating of the uncured resin.
- Excellent fracture toughness, at least 3 times greater than general-purpose epoxy, as a material cured by liquid crystal domain formation.
- Cross-linked and fixed higher-order structure, superior in fracture toughness and heat resistance.

## 3 Background of the Development

In recent years, there has been an increased demand for lower fuel consumption of moving vehicles to reduce their environmental impact, and resin composites are attracting attention as lightweight and high-strength materials. There is a demand for tougher resins as resin composite materials are susceptible to brittle fracture and have a problem with impact resistance. Investigations into toughening the epoxy resins that are widely used as matrix resins for composite materials have been made by adding rubber or elastomer, or adding an engineering plastic<sup>1), 2)</sup>. However, the former often brings about a decrease in elastic modulus and strength, and the latter causes a drop in processability due to greater viscosity, so their effect of improving toughness is limited and further improvement is required. On the other hand, it is known that toughness can be greatly enhanced by introducing a mesogenic group into the epoxy resin to form a higher order structure in the cured resin<sup>3), 4)</sup>. However, the introduction of a mesogenic group increases the crystallinity of the material and often causes problems with handling, making industrial application difficult. Therefore, Hitachi Chemical attempted to develop a liquid crystalline epoxy resin that combines excellent handling in the uncured state with high toughness as a cured product.

## 4 Technical Details

We developed a new tough liquid crystalline epoxy resin by controlling the crystallinity and molecular orientation by multimerizing mesogenic epoxy monomers via aromatic units, as shown in **Figure 1**. **Figure 2** shows the temperature-viscosity curves for the mesogenic epoxy monomer and the developed resin.

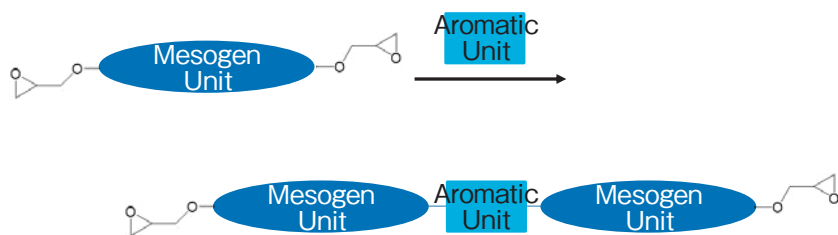


Figure 1 Modified mesogenic epoxy compounds

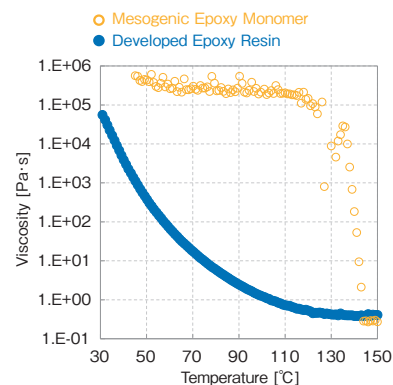
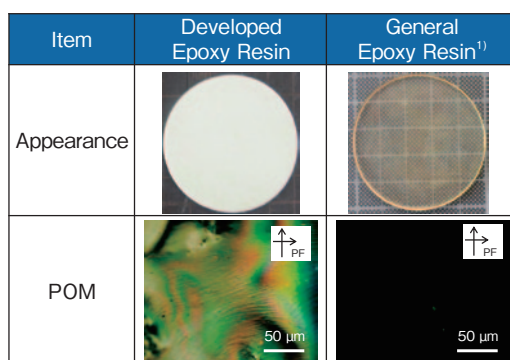


Figure 2 Temperature dependence of viscosity of monomer and developed epoxy resin

Unlike the monomer that crystallized at 130 °C or lower, the developed resin does not change phase in the temperature range of 30 to 150 °C, which makes solvent-free coating by heating easier. **Figure 3** shows the appearance of the developed resin and general-purpose epoxy resin cured with diaminodiphenylsulfone.



1) Diglycidylether of bisphenol A

Figure 3 Appearance and POM image of cured epoxy resin

The developed resin undergoes a reaction-induced phase transition to form liquid crystal domains in the cured product. The appearance became cloudy white and depolarization images were observed with the orthogonal Nicol optical system of a polarizing microscope. **Table 1** shows the properties of the developed resin and general-purpose epoxy resin cured with diaminodiphenylsulfone.

Table 1 Properties of cured epoxy resin<sup>1)</sup>

Item	Unit	Developed Epoxy Resin	General Epoxy Resin	Note
Fracture Toughness	MPa·m <sup>1/2</sup>	2.5	0.6	SENB <sup>2)</sup> Test
T <sub>g</sub>	°C	175	179	DMA
Modulus	GPa	2.7	2.8	Flexural Test
Water Absorption	%	1.6	2.4	48 h in 98 °C water

1) 150 °C 4 h, 2) Single Edge Notched Bend

Because the higher order structures formed by self-alignment are cross-linked and fixed, the developed resin exhibited an extremely high fracture structure toughness of 2.5 MPa·m<sup>1/2</sup> while maintaining high heat resistance as a thermosetting resin. Therefore, the developed resin is considered to be a suitable matrix resin for high-strength composite materials.

## 5 Future Business Development

- Investigation of applications to composite materials and development of applications

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# Study on the Conformability Expression Mechanism of Our Easy Peel-Off Films Using Relaxation Times Measurement and Molecular Dynamics Simulation

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## 1 Abstract

Easy peel-off films can be easily adhered and peeled off at room temperature, leaving no adhesive residue. Due to their convenience, demand for such films is expanding<sup>1)</sup>. An important property of these films is wettability. If wettability is good, they can follow the surface asperity of the adherend with the application of a slight force in a short time and can exhibit sufficient adherence properties. However, in order to control the wettability of the films, it is necessary to predict not only the bulk physical properties but also the behavior of the adhesives at the molecular level, and their design difficulty is high. Therefore, in this study, we developed a new analytical method that can quantify and visualize the relationship between wettability and molecular mobility by using a combination of instrumental analysis and molecular dynamic simulation.

## 2 Characteristics of the Analysis Technology

- Visualization of nanoscale molecular motions that cannot be observed directly.
- Quantification of the mobility of molecular substructures in materials.
- Prediction of product properties from molecular level behavior.

## 3 Background of the Development

Easy peel-off films are used in multiple applications, such as preventing damage during processing, storage and transportation of electronic materials, and protecting the surface of smartphones. Hitachi Chemical has developed a pressure-sensitive adhesive for easy peel-off films. Good characteristics are achieved by the use of a monomer with polyethylene oxide (EO) in the side chain. We found that the wettability of the adhesive changes when the EO chain length of the monomer is changed. However, as there is no simple proportional relationship between the EO chain length and wettability, it is difficult to control the properties.

In addition, because there was no correlation between the bulk properties and wettability of adhesives using monomers with different EO chain lengths, it was assumed that the molecular level behavior of the adhesive affects the wettability. However, this assumption was difficult to verify using conventional analytical techniques alone. Therefore, to clarify this mechanism, we tried to develop an analytical method that can visualize the relationship between wettability and molecular mobility.

## 4 Technical Details

In this study, we developed a new technique that can quantify and visualize the relationship between wettability and molecular mobility by using a combination of instrumental analysis and molecular dynamic simulation. The following shows the results of analyzing the wettability expression mechanism of adhesives for easy peel-off films using the analytical method that we developed.

1) In the molecular dynamic simulation, we created polymer drops of adhesives with different EO chain lengths and visualized their wet spreading behavior onto the adherend. The results are shown in **Figure 1**. It can be seen from **Figure 1** that the model with a short EO chain length has a more rapid initial wet spreading rate than the other models, and has better wettability. **Figure 2** shows the verification results of easy peel-off films that we actually created. When the wettability was

evaluated from the time required for the area where the film and the adherend are in close contact to spread across the adherend, it confirmed the same trend as the simulation results. Furthermore, it was found that extreme wettability values exist with respect to EO chain length.

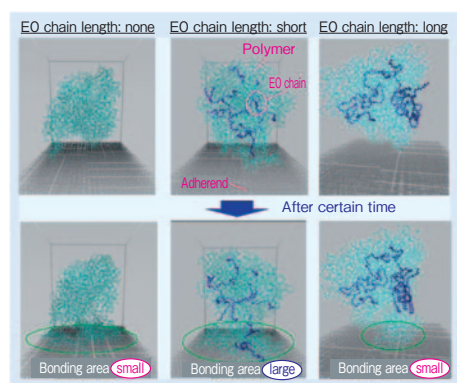


Figure 1 Analysis Result of Wetting Behavior of Adhesives to Adherent by Molecular Dynamics Simulation

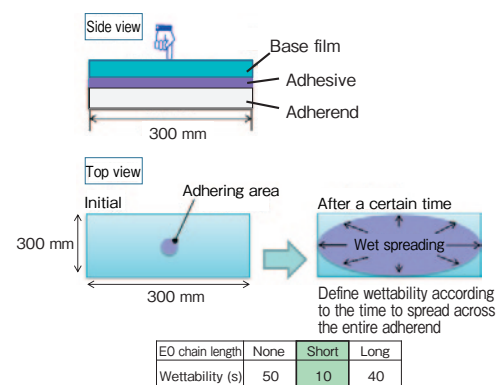
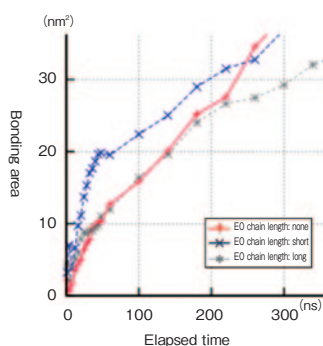


Figure 2 Performance Assessment Method and Results of Wetting Behavior of Each Adhesive

2) The nuclear magnetic resonance apparatus (NMR) can calculate the lattice-spin relaxation time for each molecular substructure. This relaxation time correlates with the mobility of the molecule. It can be said that the longer the relaxation time of the studied adhesive, the higher its molecular mobility is<sup>2)</sup>. **Figure 3** shows the change in relaxation time of each part of the EO chain when the temperature changes. From **Figure 3** it can be seen that the amount of change in relaxation time due to temperature rise varies according to the EO chain length. Suggests that the restraint state of the EO chain differs in the adhesives. This is consistent with the results of the molecular dynamic simulation. Focusing on the behavior of the EO chain in **Figure 1**, the short EO chains exist to extend into the polymer and show a behavior that promotes wet spreading of the adhesive. However, the long EO chains aggregate and exhibit behavior that inhibits wet spreading.

3) Based on molecular dynamic simulations and relaxation time measurements, the wettability expression mechanism of the studied samples is summarized in **Figure 4**.

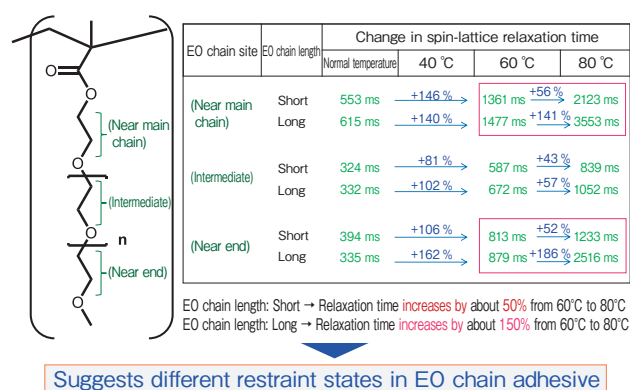


Figure 3 Measurement Results of Spin-lattice Relaxation Times of Polyethylene Oxide Chain Partial Substructures under Heating Conditions

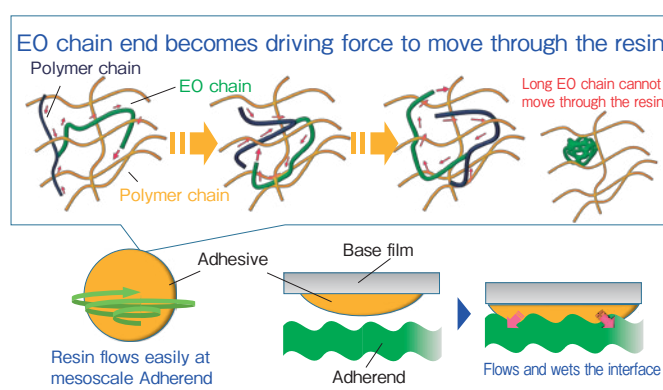


Figure 4 Mechanism of Wettability Triggered by Specific Chain Length of Polyethylene Oxide

## 5 Future Business Development

- Development of the technology using this method to various adhesives
- Establishment of the expression mechanism for other properties, such as peelability

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- 2) T.D.W Claridge: High-Resolution NMR Techniques in Organic Chemistry, Tokyo, Kodansha, Ltd., pp.13-44 (2004)

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