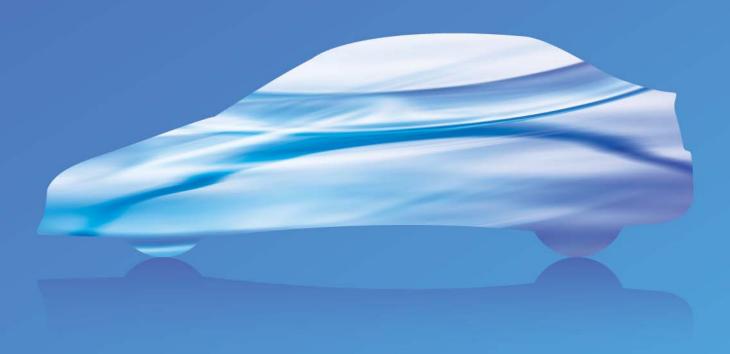
Silicone Materials for Automobiles



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Silicone Fluids and Secondary Products for Automotive Applications

The auto industry has been unremitting in its pursuit of development of automotive technologies to improve safety, comfort, and fuel efficiency. Silicones have frequently been used as automotive materials, and Shin-Etsu has been using the latest technologies to develop products to meet evolving needs. In these pages we will present examples of some typical applications, mainly featuring silicone fluids and their secondary products.

Introduction

In recent years, automakers have taken efforts to make safer vehicles that are more comfortable and eco-friendly by adding car navigation systems, sensors and other features, while making vehicles lighter and more fuel-efficient. In this article, we will discuss some of the places where silicone fluids and their secondary products (emulsions, oil blends) are used. We will also discuss auto chemicals and subsidiary materials used in the manufacture of auto parts.

1. In-vehicle materials

1-1. Sensor fill materials, damper materials KF-96

For years, dimethyl silicone fluid (KF-96) has been used as a gloss enhancer for automotive waxes, as a fill material in rubber dampers, and a damping medium in instrument meters. Today, it is used in more wide-ranging applications, as a fill material in sensors and a damping medium for auto seats.

1-2. Power transmission components (fan couplings, etc.) KF-967, KF-9006

These heat-resistant silicone fluids have enhanced oxidation stability, achieved by

adding heat-resistance improvers to dimethyl silicone fluid. They are used as fan coupling fluids and in other torque transmission applications, and as a heating medium in automobiles (Table 1).

1-3. Modifier for synthetic leather seat materials Double end-capped carbinol-modified fluids Single end-capped diol-modified fluids

Carbinol-modified siloxanes can be used to improve the slickness and texture of urethane-based synthetic leather seats. The double end-capped carbinol types (KF-6001, KF-6002, KF-6003) improve cold resistance and texture, while the single end-capped diol-modified types (X-22-176 series) improve slickness.

1-4. Weather strip coating agent X-32-1291

X-32-1291 is a solvent-based coating agent for sponge type rubber weather strips. It helps prevent wear and reduces squeaks when windows are opened and closed.

1-5. Modifier for tires and rubbers KBE-846

Tires compounded with silica are known to help boost fuel economy and provide better grip on wet roads. Unfortunately, silica-compounded tires wore out quickly and were therefore not practical. Later, KBE-846 was developed by researchers who realized that sulfide silane could be used to improve the wear life of silica-compounded tires.

1-6. Plastic & rubber modifiers

Master pellets and acrylic silicone powders Silicone master pellets are plastics compounded with highly polymerized siloxanes (30-50% by mass). Blended into plastics at roughly 0.1-2% concentration, they improve mold release properties, which helps boost molding speed. In addition, the silicone gradually bleeds out to provide a sustained lubrication effect. Acrylic silicone powders have good miscibility with PVC resin, EPDM and other synthetic resins. Also, the silicone component on the powder surface acts to improve tribological properties and provide anti-blocking properties, anti-wear properties and reduce noise created when parts rub together (Photos 1 & 2).

2. Automotive chemicals, other applications

2-1. Glass water repellents X-24-9418

The fluorosilicone water repellent X-24-9418 is fluorosilicone in an isopropyl alcohol solution. Used to treat various substrates, at

Table 1: Silicone fluids for fan couplings

Item Product name	KF-967	KF-9006				
Appearance	Tan transparent liquid	Tan liquid				
Viscosity at 25°C, mm ² /s	1,000-15,000	6,000-20,000				
Features	For closed systems Good viscosity-temperature characteristics	For closed systems Good heat resistance				
Base fluid type	Dimethyl silicone	Methylphenyl silicone				
Heat-resistance improver	Aromatic amine	Aromatic amine				

(Not specified values)

Table 2: Glass water repellents

Product name Item	X-24-9418	
Appearance	Colorless transparent liquid	
Viscosity at 25°C, mm ² /s	2.8	
Specific gravity at 25°C	0.794	
Active ingredient, %	3	
Diluent	Isopropyl alcohol	
Water contact angle*	105°	
Hexadecane contact angle*	55°	
Water fall angle*	15°	

st On glass substrate, after drying for 1 day at room temperature. (Not specified values)

Photo 1: Electron micrograph of acrylic silicone powder

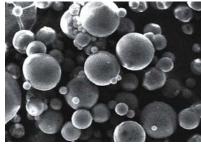


Photo 2: Silicone master pellets



Table 3: Rubber & plastic molding release agents

Product name	KM-862T	KM-740T	KM-742T	KM-722T	KM-244F
Appearance	Creamy white liquid	Creamy white liquid	Creamy white liquid	Creamy white liquid	Pale yellow liquid
Active ingredient, %	60	38	28	30	100
рН	4.0	7.0	7.2	5.0	_
Ionicity	Nonionic	Nonionic	Nonionic	Nonionic	_
Features	High viscosity dimethyl silicone emulsion	Low viscosity dimethyl silicone emulsion	Low viscosity dimethyl silicone emulsion	Medium viscosity dimethyl silicone emulsion (contains xylene)	Polyether silicone

(Not specified values)

room temperature it forms a uniform film with exceptional water repellency, oil repellency, release properties, and antifouling properties (Table 2).

2-2. Car waxes and car wash detergents

Dimethyl silicone fluid (KF-96) has long been used as a gloss enhancer for car body waxes, and more recently as a tire gloss enhancer. For certain applications, it is mixed with fluids containing high-molecular-weight silicone resin (KF-9021, KM-9717) or acrylic silicone (X-22-8000, -8100 series) to improve film durability.

In car wash machines, the wax component is often an amino silicone emulsion or other silicone with amino groups, which improve adsorption onto car body panels. (Polon MF-14EC, X-52-800 series)

2-3. Tire & hose mold release agents, aluminum die-casting release agents

Silicone emulsions are used as release agents

Table 4: Aluminum die-casting release agents

Product name	X-22-1877	X-52-8051	Silcast U
Appearance	Pale yellow transparent liquid	Creamy white liquid	Creamy white liquid
Active ingredient, %	100	50	32
Features	Alkyl-aralkyl silicone	Alkyl-aralkyl silicone Weakly ionic emulsion	Alkyl silicone Weakly ionic emulsion

(Not specified values)

when molding tires, radiator hoses, fuel hoses, and other rubber parts (Table 3). Alkylor alkyl-aralkyl-modified silicone fluids (or their emulsions) are used as release agents for aluminum die-casting (Table 4).

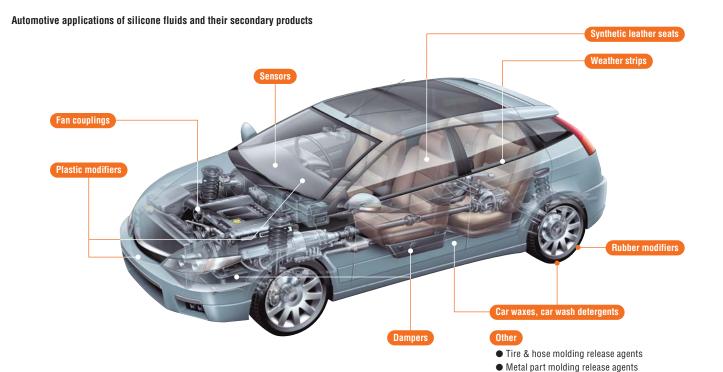
Conclusion

Automobiles are complex machines manufactured using advanced plastics and fabrics, and sophisticated mechanical, electric and electronic components. These parts have to last ten years or more. Most of the materials that are currently under development or that have been used for

automotive applications have been developed in cooperation with automakers and auto parts manufacturers, and Shin-Etsu is simply not at liberty to discuss them in this publication.

Without question, specially designed silicones will continue to be used in places with unique requirements. Shin-Etsu is committed to development of materials that meet diverse user needs, and we look forward to hearing your ideas and requests in this regard.

• Information current as of Jan. 2007.



Silicone Elastomers for Automotive Applications

With the quest for higher performance automobiles and the increased use of electronic components, the performance requirements for silicones and other raw materials are becoming ever more diverse and sophisticated. In this article, we will present liquid silicone rubbers designed for automotive applications, for the fixing and protection of parts, thermal interface, and other functions.

Introduction

As automobiles have become higher performance products, the use of electronic components has also increased. In some models today there are over 70 Electronic Control Units (ECU); silicone elastomers are used as sealing materials, adhesives and potting agents for these ECUs. Silicone elastomers provide exceptional durability and stable performance over a wide temperature range. In this article, we'll focus on car electronics as we present a number of liquid silicone rubber products.

1. Protecting components

In this section, we will discuss products designed for the protection of automotive components, including conformal coatings, potting materials and sealing materials, plus products designed to prevent sulfurization, which are attracting interest throughout the industry today.

Conformal Coatings

Conformal coatings are dielectric materials applied to electric and electronic components to protect from moisture, condensation and dust. Shin-Etsu has developed eco-friendly solventless products and low- and high-viscosity types. Different products can be applied in different spots,

as needs dictate (Table 1).

Potting Materials

Like conformal coatings, potting materials protect electronic components arranged on circuit boards from moisture, condensation and dust. Potting also helps reduce mechanical stress on electronic components caused by extreme temperatures and vibration. Regular silicone is called dimethyl silicone, and it features methyl groups attached to the side chains of the polymer. This type of silicone cannot be used in places where it will be directly exposed to gasoline or oils, but this weak point can be overcome by introducing trifluoropropyl groups into the side chains of the base polymer (Table 2).

Case Seal Materials

Case seal materials are used for waterproofing, to protect the electronic components inside ECUs from damage. These silicones will be exposed to the outdoor elements for years, and thus must provide high bonding durability. Using proprietary technology, Shin-Etsu has also launched low-temperature-cure products, designed to help improve productivity and for use with a wider variety of substrate materials. What's more, by adding substances that capture acidic gases from auto exhausts, which include NOx and SOx, we have

developed silicones that help ensure the performance of components over years of use (Table 3).

2. Thermal Interface Materials

The transistors and ICs on circuit boards generate considerable heat. Silicones with high thermal conductivity are used to effectively radiate this heat. Because these silicones are applied directly to electric and electronic components, they have been designed with minimal amounts of low-molecular-weight siloxane, since this substance can cause faulty conduction at electrical contacts. Our lineup of thermal interface materials includes greases, adhesives and sheets. The properties of some typical thermal interface adhesives are shown in Table 4.

3. Fastening of parts

Many adhesives are used for the fastening of electronic parts and structural bonding. Some usage locations stay continually hot, while others are exposed to gasoline and other substances. Shin-Etsu has developed a lineup of adhesives to meet the requirements of diverse applications and manufacturing processes, so the user can select a product of the appropriate cure type for their specific needs (see 4. Curing mechanisms).

Table 1: Conformal coatings

Product name Item	KE-1870	KE-1871	KE-3470	KE-3420
Viscosity, mPa·s	400	800	70	700
Cure type	Addition	Addition	Condensation (acetone)	Condensation (acetone)
Cure conditions	0.5h/150°C	0.5h/150°C	23°C/50% RH 7 days	23°C/50% RH 7 days
Hardness, Durometer A	15	27	35	19
Volume resistivity, $T\Omega \cdot m$	10	10	20	60
Relative dielectric constant, 50Hz	3.1	3.1	3	3
Dielectric dissipation factor, 50Hz	1.0×10 ⁻³	1.0×10 ⁻³	0.1×10 ⁻³	3.0×10 ⁻³

(Not specified values)



Electronic components potted with silicone gel

Table 2: Potting materials

Product name		FE-57	KE-1842	KE-200 CX-200
	Addition	Addition	Addition	Condensation (acetone)
	Cold-resistant transparent gel	Cold-resistant transparent gel	Low hardness	Reduced low- molecular- weight siloxane Rapid cure
Consistency	Liquid	Liquid	Low viscosity	Liquid
Color	Slightly hazy	Light brown	White	Blue transparent translucent Pale yellow
mPa·s	800	2000	4000	2800
g/cm³	0.99	1.28	1.00	1.01
	0.5h/130°C	2h/125°C	1h/120°C	72h/23°C
	90	60	_	_
Hardness, Durometer A		_	10	25
Volume resistivity, $T\Omega \cdot m$		0.02	1	60
Dielectric breakdown voltage, kV			20	20
Relative dielectric constant, 50Hz		7.0	3.5	2.9
tion factor, 50Hz	2×10-4	1×10-2	5×10 ⁻³	2×10-3
	Consistency Color mPa·s g/cm³ meter A ity, ΤΩ·m own voltage, kV constant, 50Hz	Addition Cold-resistant transparent gel Consistency Liquid Color Slightly hazy MPa·s 800 g/cm³ 0.99 0.5h/130°C 90 meter A — ity, ΤΩ·m 10 own voltage, kV 15 constant, 50Hz 2.9	Addition Addition	Addition Addition Addition

(Not specified values)

Table 3: Case seal materials

Item	Product name	KE-1833	10-SEAL-300	X-32-2582A/B
Cure type	9	Addition	Addition	Addition
Features		Heat-resistant adhesive	Captures SOx & NOx	Room-temperature cure
Appearance (after cure)		Reddish brown	White	Creamy white translucent
Viscosity	, Pa·s	140	60	A 360 B 850
Density,	g/cm ³	1.34	1.23	1.07
Hardness	s, Durometer A	33	30	25
Elongation at break, %		350	250	610
Tensile st	trength, MPa	3.4	2.0	3.7
0.1	Glass	1.8	1.5	1.5
Shear adhesive	Aluminum	1.8	1.5	1.9
strength	PBT (fiber reinforced)	1.8	1.5	1.5
	PPS (fiber reinforced)	1.8	1.5	1.9
Cure con	ditions	1h/120°C	1h/100°C	24h/room temp.

(Not specified values)

Table 4: Thermal interface adhesives

Item	Product name	KE-3466	KE-3467	X-32-2020	KE-1867
Cure type		Condensatio	on (acetone)	Add	ition
Features		Reduced low- molecular- weight siloxane UL certified	Reduced low- molecular- weight siloxane UL certified	Reduced low- molecular- weight siloxane	Reduced low- molecular- weight siloxane UL certified
Annogranco	Consistency	Med. viscosity	High viscosity	High viscosity	Med. viscosity
Appearance	Color	White	White	Gray	Gray
Viscosity, Pa-s		45	80	100	70
Density, g/cm ³		2.80	2.95	2.83	2.92
Cure conditions		23°C/50% RH 7 days	23°C/50% RH 7 days	1h/120°C	1h/120°C
Hardness, Dur	ometer A	85	90	78	75
Tensile strength	n, MPa	3.1	3.6	1.6	1.2
Elongation at break, %		30	30	30	70
Volume resistivity, $T\Omega \cdot m$		2.9	2.5	1.0	1.2
Dielectric breakdov	wn voltage, kV/mm	24	25	23	23
Thermal condu	ctivity, W/m·K	1.9	2.4	1.8	2.1

(Not specified values)

4. Curing Mechanisms

There are four types of curing mechanisms for silicone elastomers, each with distinctive characteristics (Table 5).

Addition-cure products

Generally, the cure temperature is around 120°C and cure time around one hour. Recently, manufacturers are working to develop products that cure more rapidly and at lower temperatures. Virtually no byproducts are released during the curing reaction.

Dual-cure products

A drawback of addition-cure products is that tin, nitrogen, phosphorus and sulfur compounds

can interfere with curing. To address this, Shin-Etsu developed dual-cure products based on a combination of platinum addition/peroxide cure.

Condensation-cure products

These products cure by reacting with moisture in the air so that, unlike with addition-cure products, heating devices are unnecessary. These products are grouped according to the type of gas released in minute quantities during the cure reaction. Acetone-cure (i.e. acetone is released) and alcohol-cure types are used for electric and electronic applications. Generally, curing takes seven days, at 23±2°C and 50% relative humidity, but some products cure

in as little as one to three days.

UV-cure products

These products cure rapidly through irradiation with UV light.

Conclusion

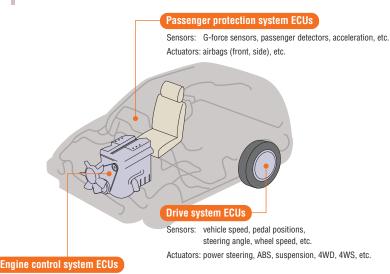
In the field of automotive components and materials, there is steadily growing demand for products that offer greater functionality and environmental performance. Shin-Etsu is committed to ongoing development of materials to meet this demand, and we'd like to hear from our customers regarding any ideas and requests they may have.

• Information current as of Apr. 2007.

Table 5: Cure mechanism & characteristics

Cure mechanism		Cure temp.	Cure time	Advantages	
	1-component		80°C or higher	about 60 min	Rapid cure
Addition	2-component		Room temp. or higher	1-3 days	Heating unnecessary (rapid cure)
Dual-cure		150°C or higher	about 60 min	Resists cure inhibition	
	1-component	Acetone	Room temp.	7 days	
Conden-	1-component	Oxime			
sation		Acetic acid			unnecessary
	2-component	Alcohol	4.0 days		
	2-component	Acetone		1-3 days	
IIV-cure	IV-cure Acrylic Mercapto		Room temp.	20 sec	Heating unnecessary
ov cure			rtoom temp.	20 366	(rapid cure)

Application of silicone elastomers in the field of automotive electronics



Sensors: temperature, pressure, flow rate, crank position, oxygen, NOx, water temperature, etc. Actuators: air flow, injectors, valve timing, etc.

Silicone Elastomers for Automotive Applications — Application to Airbags —

Of all automotive technologies, those designed to help keep drivers and passengers safe in the event of an accident are among the most critical. The properties of silicone materials have led to their use in numerous locations in modern vehicles. This article will look at the use of silicones in automobiles, with a particular focus on safety.



Introduction

There were over 850,000,000 cars on the world's roads in 2004. With growth in the Chinese market, this number is expected to reach 1.2 billion by the year 2020*1. In automobiles, silicone elastomers have long been used to manufacture spark plug boots and connector seals, and more recently for such components as intake manifold gaskets (fluorosilicone), turbo charger hoses and silicone wiper blades.

A look at the trends*1 in research and development of automotive materials reveals that, in addition to the quest for vehicles that are lighter and more efficient and for new sources of power - collectively aimed at reducing CO2 emissions - automakers are also working to make vehicles safer. In the next section, we will discuss the connection between silicone elastomers and car airbags.

1. Airbags

The first airbags were installed in vehicles in the 1960s. Airbags were developed to reduce head injuries to passengers wearing seatbelts in the event of a crash, specifically by mitigating secondary impacts (primary impact is that of the vehicle hitting another object, and the secondary impact is that of the passenger's body hitting the steering

wheel, instrument panel, windshield, etc.) *2. In recent years, industry focus has shifted to auto airbags made of 6,6-nylon, 6-nylon, polyester and other fabrics coated with silicone rubber. The silicone rubber coating materials are typically dissolved types, which are millable or liquid silicones dissolved in a solvent, or emulsions. However, in the interest of enhancing the properties required for airbag applications and reducing environmental impact, manufacturers are gradually switching to solventless silicone materials (Table 1). Curtain airbags, which are fitted in spaces along the roof extending back from the front pillars, have to maintain inflation for a longer period than the airbags installed in the driver and front passenger seats. Curtain airbags are designed to protect the head and help keep passengers from being ejected from the vehicle in the event of an impact or rollover. The manufacture of curtain airbags requires liquid silicone rubber coating agents that have characteristics of low viscosity, high strength, high adhesiveness, moisture resistance, heat resistance, low-temperature flexibility, and stability over time.

2. Viscosity / strength

The strength of silicone rubbers can be enhanced by adding a larger proportion of silica filler or increasing the polymerization of the organopolysiloxane polymer. Normally, silicones are compounded with fumed silica to improve strength, because it is not possible to obtain strength sufficient for industrial products with siloxane polymers alone*3. See Table 2 for the correlation between silica fill content and viscosity/tear

Increasing the silica fill ratio has a mechanical "volume effect", and a physicochemical "surface effect" (improved adsorption of the organopolysiloxane molecules to the particle surface, and increased intermolecular force, or chemical bonding of organopolysiloxane molecules to silanols on the silica surface), resulting in increased tear strength (Fig. 1).

Meanwhile, Table 3 illustrates the relationship between viscosity and tear strength, as affected by organopolysiloxane polymerization. With increased polymerization of the polymer, high tear strength can be achieved, but it causes uneven crosslinking (maldistribution) known as "knock tear."

Table 1: Silicone rubber coating materials

Type	Millable/ Liquid silicone solution	Emulsion	Solventless silicone
Rubber strength	•	X	•
Environmental properties	X	•	•
Workability	X	•	•

Table 2: Correlation between silica fill content and viscosity/tear strength

Sample	Sample 1	Sample 2	Sample 3
Silica content	Low	Medium	High
Organopolysiloxane	Medium chain	Medium chain	Medium chain
Viscosity	Low —		→ High
Tear strength	Low —		→ High

Table 3: Correlation between polymerization of organopolysiloxane and viscosity/tear strength

Sample	Sample 4	Sample 5	Sample 6
Silica content	Medium	Medium	Medium
Organopolysiloxane	Short chain	Medium chain	Long chain
Viscosity	Low —		→ High
Tear strength	Low —		→ High

As Tables 2 and 3 show, with increased strength there is an increase in viscosity. But to enable high-speed application of coating materials, researchers must develop low-viscosity/high-strength technologies.

Furthermore, when applying coating materials at high speed, the shear viscosity of the coating material is largely influenced by the application conditions. Figure 2 shows the viscosity behavior of Sample 2 and Sample 3 (shown in Table 2) at different shear speeds. It is essential that the composition of the coating material be designed such that shear viscosity meets the requirements of the coating conditions.

3. Adhesiveness

The next important consideration for an airbag coating is the adhesion of the coating to the fabric. Silane coupling agents can be used to obtain the desired adhesive properties for proper adhesion to the fabric. The structure of a silane coupling agent is

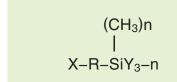
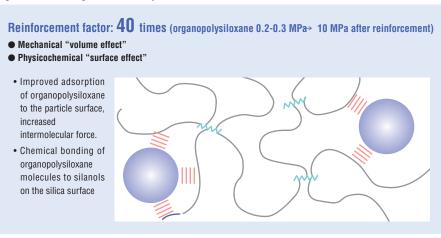


Figure 1: Reinforcing effect of silica particles



typically like that shown in the following structural formula*4.

"X" represents an organic functional group, and "Y" a hydrolyzable group.

The organic functional group "X" reacts with or promotes miscibility with organic materials. Various types of functional groups are synthesized.

Meanwhile, for the hydrolyzable group "Y", there are a number of possible functional groups, but the methoxy groups, ethoxy groups and alkoxy groups are most commonly used.

Silane coupling agents, whose molecules contain functional groups, thus act as an adhesive auxiliary agent for better adhesion to fabrics. This is thought to be the effect of hydrogen bonding, or wetting, or miscibilization (Fig. 3).

Figure 3:

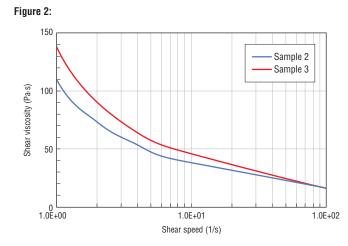
Conclusion

In the field of automotive components and materials, there is steadily growing demand for products that offer greater functionality and environmental performance. Shin-Etsu is committed to ongoing development of materials to meet this demand, and we'd like to hear from our users regarding any ideas and requests they may have.

● Information current as of Jul. 2007.

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Silicone rubber

Y: hydrolyzable group

Thermal Interface Materials for Automotive Applications

Car electronics has progressed on a course that should lead to improvements in performance in terms of safety, comfort and the environment. As electronic devices become smaller in size and higher in performance, thermal interface materials have become a more and more important theme. Among silicone materials for heat dissipation, this paper discusses those developed for automotive applications, for which performance requirements are especially strict.

Introduction

At the same time that the automobile grows more and more sophisticated in performance, extremely rapid progress is also being made in the electronification of automotive parts. And as electronic devices become more compact and more tightly integrated, the volumes of heat generated from them have risen dramatically. In consequence, materials that provide outstanding thermal performance have come into strong demand. Automobiles are used in extreme environments ranging from deserts to arctic regions, and are exposed to vibrations. It is imperative, therefore, that thermal interface materials show durability against heat, cold and vibrations. As a material that can satisfy these requirements, silicone is ideal, and silicone thermal interface materials have proven to be highly reliable in automotive

Table 1: Properties and Applications of Silicone Thermal Interface Materials

Property	Type	Applications
		Power transistor heat dissipation and insulation
	Thermal conductive	Power module heat dissipation and insulation
leet-shaped moldings	sheet	Insulation and thermal conducting media in temperature sensing components
Sheet-shaped moldings	Low-hardness thermal conductive sheet	Semiconductor device heat dissipation and insulation
Phase change sheet		Thermal conducting media between heat-emitting elements and cooling materials
	The second second section	Power module heat dissipation
/ tions	Thermal conductive grease	Heat dissipation from heat-generating ICs
Past	9.000	Semiconductor device heat dissipation
Pasty compositions	Thermal conductive gel, adhesive	For fixing heat dissipation from electronic components, for bonding

Table 2: Pump out tests

Cycle count	Newly developed product	Conventional product
Initial period (0 cycle)		
149 cycles		
457 cycles	0	

applications. In light of this background, silicone thermal interface materials developed especially for automotive applications will be introduced.

1. Silicone Thermal Interface Materials

Silicone thermal interface materials start with a base of silicone polymer, which means they outperform other organic polymers in terms of heat and cold resistance, weatherability and electrical properties. These special silicone products excel in long-term reliability and are thus used as thermal interface materials in a wide array of applications. The products are available in sheet form and as paste compositions, and which is used will depend on the intended application (Table 1).

2. Thermal Interface Grease

Initially, there were many cases in which automakers used thermal conductive grease that can be applied in mass-production methods based on automation.

Recently, however, the performance requirements for such thermal conductive grease have been getting much stricter.

In addition to improvements in the rate of thermal conductivity, demand has arisen for thermal conductive grease that exhibits no bleed out or pump out phenomenon. Given that such grease is a simple mixture of polymer and thermal conductive filler, depending on how it is used, it can gradually

Photo 2: TC-SP-1.7 Series



manifest pump out due to cold or heat shocks or other conditions. Consequently, this type of grease has the disadvantage that its thermal performance sometimes suddenly becomes very poor. Nevertheless, given the product characteristics of this grease, it is extremely difficult to eliminate bleed out or pump out phenomenon altogether. Nevertheless, this hurdle is being overcome thanks to recent advances in research. Let us consider an example. Table 2 presents the results of pump out tests performed on the very latest thermal conductive grease products to be developed and on conventional predecessors. In the conventional products, as the number of heat cycles advances, pump out and bleed out are slowly produced. In the very latest products, on the other hand, we see that there is absolutely no change in configuration from the initial state. Newly developed grease that exhibits this property does not require any additional heat processing after it has been applied as a coating, and it demonstrates highly stabilized performance. Another advantage of the latest grease products is that in comparison to conventional sheet-formed thermal materials, they are much softer, so there is no need for concern about damage to electronic devices resulting from stress.

3. Thermal Interface Sheets

Thermal interface sheets are categorized into three types: high-hardness rubber thermal interface sheets, low-hardness rubber thermal interface sheets, and phase-change materials that soften when heated. Here, we would like to introduce the latest products developed by Shin-Etsu.

The TC-CA Series was developed using

Figure 1: Structure of TC-SP-1.7 Series

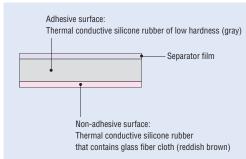




Photo 1: TC-CA Series

Shin-Etsu's proprietary polymer technology and filler compounding technology. These low-hardness rubber thermal interface sheets provide both high thermal conductivity and excellent electrical properties. Their low hardness also gives them good compressibility and stress-relieving properties, plus excellent processing characteristics, working properties and reworkability. Another major feature is their advantage in cost performance compared to conventional low-hardness products (Photo 1, Table 3. Table 4).

The TC-SP-1.7 Series is a line of adhesive sheets which are ultra-soft adhesive sheets, which makes them and are thus highly effective as thermal interface materials. The non-adhesive face is reinforced with glass fiber, so the sheets have outstanding physical strength and dielectric reliability, and excel in ease of application and processing characteristics. Products in this series are now being used in the electrical systems of hybrid vehicles (Photo 2, Figure 1, Table 5). Products in the PCS-LT-30 Series are described as phase-change materials. They consist of an adhesive substance (polymer) that is solid at room temperature, but undergoes phase change (softens with heat) at high temperatures. The polymer is compounded with a high proportion of thermally conductive fillers and manufactured in sheets (Table 6). These sheets outperform conventional products in various ways: 1) They can be applied to devices of varying

Table 3: General Properties

Product name	TC-100CAS-10 "100" shows 1.0 mm in thickness.	TC-100CAB-10 "100" shows 1.0 mm in thickness.	TC-100CAD-10 "100" shows 1.0 mm in thickness.	TC-100CAT-20 "100" shows 1.0 mm in thickness.
Appearance	Dark gray	Pink	Light reddish purple	Gray
Sheet size	300×400	300×400	300×400	300×400
Structure	Single layer	Single layer	Single layer	Single layer
Density, g/cm ³	1.9	2.2	3.0	3.2
Hardness, Asker C	10	10	10	20
Dielectric breakdown voltage, 1mm, kV	22	22	15	15
Thermal conductivity*1, W/m·K	1.8	2.3	3.2	4.5
Thermal resistance*2, °C/W	0.65	0.49	0.43	0.32
Flammability, UL94	V-0 equivalent	V-0 equivalent	V-0 equivalent	V-0 equivalent
Thickness, mm	0.5, 1.0, 1.5, 2.0, 2.5 3, 4, 5, 6, 7, 8, 9,10	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5	0.5, 1.0, 1.5, 2.0 2.5, 3, 4, 5
Operating temp. range, °C	-40 to 150	-40 to 150	-40 to 180	-40 to 180

^{*1} Based on ISO-22007-2 *2 Based on Shin-Etsu method (Thickness: 1 mm)

(Not specified values)

Table 4: Conventional Products

Conventional products	TC-HSV-1.4	TC-THS	TC-TXS
Thermal conductivity*, W/m·K	1.2	2.1	3.3

* Based on ISO-22007-2

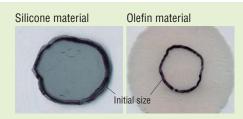
(Not specified values)

heights, providing a "leveling effect" by filling gaps of uneven size (Figure 2); 2) They provide improved resistance to pump-out (i.e. they don't become fluid even at high temperatures) (Photo 3); and 3) They have good transfer properties for greater ease of

Conclusion

Silicone thermal interface materials have come into widespread use in all types of equipment power supplies, as well as in computer CPUs and chip sets. In recent years, moreover, progress has been made in

Photo3: Pump out in silicone versus olefin materials



Inserted with clip via glass plate at a tightening force of 0.9 kg and subjected to thermal application thermal compression bonding at 70°C per hour. Heat cycle was repeated once every 10 minutes (25 times) from 125 to 55°C and the spread of phase change sheet was checked.

(Not specified values)

wide-area mounting of heat-dissipating components associated with car electronics. With demand in the hybrid and electric vehicle seaments expected to arow in the coming years, Shin-Etsu will intensify efforts to develop new products and technologies based on ideas and insight gained from your feedback as users

Information current as of Jul. 2010.

Figure 2: Image of Phase-change

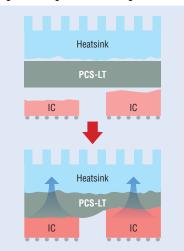


Table 5: General Properties of TC-SP-1.7 Series

Product Item	t name	Test method	TC-100SP-1.7
External appearance, Color tone		_	Gray/Reddish brown
Thickness,	mm	_	1.0
Density,	g/cm ³	JIS K 6249	2.32
Hardness*1, Asker C		_	2
Thermal conductivity,	W/m·K	ASTM E 1530	1.7
Thermal resistance*2,	K/W	Shin-Etsu measurement method	1.00
Insulation breakdown voltage,	kV	JIS K 6249	20
Flame retardancy		UL94	V-0
Standard sheet thickness,	mm	_	0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0

^{*1} Measurements taken with 2 overlapping sheets of 6-mm sheet of low hardness.

*2 Model heater (TO-3P type, 7 cm2), applied power: 28 W/Load 29.4 kPa (300 gt/ cm2)

Table 6: General Properties of Phase Change Material

Product name	PCS-LT-30
Color	Gray
Initial thickness, µm	120
Bond line thickness*2,3, µm	28
Density at 25°C, g/cm ³	2.4
Softening point*4, °C	48
Thermal conductivity*1, W/m·K	3.0
Thermal resistance*1,3, cm ² ·K/W	0.11
Sheet size, mm	300×400
*1 Measured by laser flash method.	(Not specified values)

^{*1} Measured by laser flash method.

*2 Measured by Micro gauge.

- *3 After 1 hour compression, 200 psi/100 °C.
- *4 Measured by Shin-Etsu method

LIMS Materials for Automobiles

Liquid silicone rubber LIMS materials have attracted wide attention because they can facilitate stepped-up rationalization of formation processes. Advances are also being made in the use of such materials for automobiles. In particular, products have been developed in which siloxane of low molecular weight has been removed. This eliminates the need for secondary curing to remove such siloxane. Accordingly, LIMS materials can be expected to find more widespread applications in automobiles, for which there are very strict requirements for stabilized performance.

Introduction

Silicone elastomers are used in various automotive parts because they are advantageous in terms of heat resistance, low-temperature characteristics and electrical characteristics. Meanwhile, thanks to technological innovations in molding machines, metal molds and materials, conventional millable or high consistency rubber is being replaced with liquid-type LIMS (Liquid Injection Molding System) materials, which facilitate rationalization of molding.

The physical properties of cured substances obtained by LIMS molding are in no way inferior to those of millable rubber, and LIMS molding facilitates injection molding at low pressure. Moreover, with advances made in molding machines and metal molds, molding cycles have been shortened. Still another advantage is that products are flashless and runnerless, so waste produced during molding has declined.

This paper introduces materials recently developed using LIMS, for which there is no need for secondary curing.

1. Features of Liquid Silicone Rubber LIMS Material

1. Outstanding material characteristics

These materials offer a number of outstanding characteristics including high strength, heat resistance and electrical insulation. They also have excellent transparency, so they can be easily colored with pigments, resulting in vividly colored mold products.

2. Reduced processing times

Because liquid silicone rubber can be cured by means of addition reaction, the time periods required for curing and molding can be shortened.

3. Improved productivity

Molding can be executed at low injection pressure and precision components can be produced. High-quality molds can be realized at good efficiency and with no contaminants.

4. Automation of molding

This material facilitates flashless and runnerless molding. It also allows molding processes to be automated, since products can be easily demolded after curing.

5. Eco-friendly

Eco-friendly molding is made possible because there are no curing reaction byproducts and no need to dispose of molding waste materials.

2. Materials of Minimal Low-Molecular-Weight Siloxane

The silicone rubber products used around electrical and electronic equipment can damage electrical contact points through volatilization of any low-molecular-weight siloxane that remains in mold products (Fig. 1). Normally, therefore, secondary curing is performed, using ovens, so as to remove low-molecular-weight siloxane before application.

LIMS materials of minimal low-molecular-weight

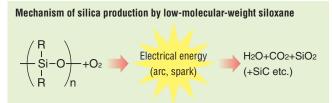
siloxane are a type of material in which low-molecular-weight siloxane has been reduced, without secondary curing, to a level comparable to that in millable rubber after it has been cured at 200°C for 4 hours

Table 1 lists products for which secondary curing is not required (KE-2019 series).

3. Applications to Harnesses

The harnesses used with vehicle-mounted electrical components make up an indispensable wiring system that transmits energy and diverse types of information. In the wake of recent advances toward high performance in automobiles, harnesses now come in a much wider array of types, and

Figure 1:Low-molecularweight siloxane



■ LIMS materials of minimal low-molecular-weight siloxane Table 1: General purpose, high strength type

Item	Product name	KE-2019-30A/B	KE-2019-40A/B	KE-2019-50
Viscosity (0.9S-1) at 23°C A/B,	Pa⋅s	300/320	340/340	900/920
130°C:MDR T10/T90,	S	31/84	33/61	23/44
Density,	g/cm ³	1.11	1.12	1.14
Hardness, Durometer A		33	42	52
Tensile strength,	MPa	6.9	10.1	11.1
Elongation at break,	%	630	570	580
Tearing strength, Angle shape,	kN/m	20	29	35

%

ppm

20

50

26

50

80 (Not specified values)

25

Table 2: Oil-bleed type

Compression set, 150°C/70h,

labio E. Oli bioda typo				
Item	Product name	KE-2017-30A/B	KE-2017-40A/B	KE-2017-50A/B
Viscosity (0.9S-1) at 23°C A/B,	Pa⋅s	1500/1500	1500/1300	2000/1600
130°C:MDR T10/T90,	S	41/77	35/70	30/60
Density,	g/cm ³	1.13	1.13	1.14
Hardness, Durometer A		32	42	52
Tensile strength,	MPa	9.1	9.2	9.5
Elongation at break,	%	740	600	500
Tearing strength, Angle shape,	kN/m	23	30	35
Compression set, 150°C/70h,	%	18	15	20
Low-molecular-weight siloxane ΣD_3 -D10	o, ppm	100	50	80

^{*} Curing conditions: Press curing at 150°C /10 min.

(Not specified values)

Low-molecular-weight siloxane ΣD₃-D₁₀, * Curing conditions: Press curing at 150°C /10 min.

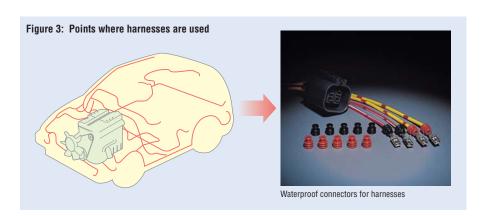
their performances greatly impact upon reliability (Fig. 3).

Thanks to progress in car electronics, demand for harnesses has trended upward. At the same time, LIMS, which does not require secondary curing, is finding more widespread use in harnesses so as to bolster reliability and production efficiency. Listed in Table 2 are oil-bleed type products used in harnesses.

4. Selective Self-adhesive LIMS Materials

Selective self-adhesive LIMS materials, which do not adhere to metal dies but only to plastic, can be used with plastic to form integral molds. Additionally, they allow molding at low pressure, so they can yield moldings in which resin deformations are minimized. What is more, the level of precision in mold products can be easily elevated. Up till now, however, it has not been possible to raise the temperature in secondary curing because plastics suffer from inadequate present problems in heat resistance. In many cases, therefore, it has been impossible to adequately remove low-molecular-weight siloxane. But with selective self-adhesive LIMS materials of minimal low-molecular-weight siloxane, this problem has been resolved. High-strength LIMS materials are given in Table 3. Table 4 lists oil-bleed type products for use as harnesses in which free oil exudes from product surfaces.

Figure 2: Comparisons of low-molecular-weight siloxane volumes based on solvent extraction method 100000 Press cured _ow-molecular-weight siloxane volume (ppm) ■ 150°C/1h 10000 ■ 200°C/4h 1000 100 10 KE-941-U KE-1950-40 KE-2017-40 (General purpose type) (General purpose LIMS material) (LIMS material of minimal low-molecular-weight siloxane)



■ Selective self-adhesive LIMS materials of minimal low-molecular-weight siloxane Table 3: General purpose, high strength type

Item	Product name	KE-2091-30A/B	KE-2091-40A/B	KE-2091-50A/B
Viscosity (0.9S-1) at 23°C A/B,	Pa⋅s	700/1800	850/2000	700/2400
120°C:MDR T10/T90,	S	20/44	19/37	21/38
Density,	g/cm ³	1.13	1.13	1.14
Hardness, Durometer A		33	43	52
Tensile strength,	MPa	9.1	11.7	11.5
Elongation at break,	%	740	680	620
Tearing strength, Angle shape,	kN/m	20	33	40
Compression set, 150°C/70h,	%	28	29	35
Low-molecular-weight siloxane ΣD_3 -D10	, ppm	150	130	160

* Curing conditions: Press curing at 150°C /10 min.

(Not specified values)

Table 4: Oil-bleed type

Item	Product name	KE-2018-30A/B	KE-2018-40A/B	KE-2018-50A/B
Viscosity (0.9S-1) at 23°C A/B,	Pa⋅s	1500/1500	1600/1400	1500/1300
120°C:MDR T10/T90,	S	22/58	23/40	25/50
Density,	g/cm ³	1.14	1.13	1.13
Hardness, Durometer A		31	42	52
Tensile strength,	MPa	9.4	10.1	9.8
Elongation at break,	%	780	680	560
Tearing strength, Angle shape,	kN/m	23	30	35
Compression set, 150°C/70h,	%	18	15	20
Low-molecular-weight siloxane ΣD_3 -D10	, ppm	170	120	180

* Curing conditions: Press curing at 150°C /10 min.

(Not specified values)

5. Prospective Benefits

Because low-molecular-weight siloxane has been minimized, metal dies will suffer much less contamination during molding and they will have to be cleaned far less frequently.

LIMS materials are eco-friendly, since the volume of low-molecular-weight siloxane produced by volatilization during curing is minimal. What is more, fluctuations in contraction rates during molding have been reduced, making it possible to realize high-quality mold products.

Conclusion

Eco-friendly products have been attracting more and more attention recently. Against this backdrop, great expectations have been put on LIMS materials because they eliminate the need for disposal of waste materials and the need for removal of low-molecular-weight siloxane through secondary curing.

LIMS materials can be expected to find applications in a diverse array of fields.

Information current as of Jan. 2008.



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