

New Products Developed Using Environment-Friendly Elastomer Rubber

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ABSTRACT Elastomer rubber products are widely used in industry, making use of their many superior properties including flexibility, resilience, elasticity, and absorption of impact and vibration. Another advantage of elastomer rubber is that the use of various additives can result in enhanced functionality over the basic characteristics. Furukawa Electric produces and markets a broad range of elastomer rubber-based products for electrical and electronic equipment and the fields of architecture and civil engineering--areas in which there has been an increasing demand in recent years for products that are environment friendly--halogen-free and flame retardant. This paper reports on the development of a halogen-free flame-retardant tape to replace conventional PVC tape, and halogen-free flame-retardant thermally conductive sheet.

1. NON-HALO (HALOGEN-FREE) F-CO TAPE

1.1 Introduction

Because of its electrical insulating properties and flexibility, tapes made from polyvinyl chloride (PVC) have long been in general use, both as insulation and in various protective applications. But since PVC includes chlorine, it can, when incinerated, produce dioxins as well as chlorine gas, and the lead used as a stabilizer constitutes a further danger of environmental pollution. These problems have therefore led in recent years to a strong, through not legislatively mandated, movement toward chlorine-free vinyl. Specific examples include restrictions on the use of toxic materials embodied in the Green Government Office Policies of the Ministry of Land, Infrastructure and Transport, and the adoption by the Ministry of Health, Labour and Welfare of halogen-free cables.

For our part, Furukawa Electric has developed a flame-retardant tape that is halogen-free and contains no lead or other heavy metals as an environment-friendly replacement for PVC tape.

1.2 Tape Development Targets

The main targets in developing a halogen-free tape to replace the PVC product may be summarized as follows:

1.2.1 Physical Targets

The most compelling advantage of PVC tape is that anyone with moderate strength can produce adequate elongation during wrapping, and, when finished, can easily tear off by hand. Thus any replacement must be able to provide:

- 1) Balanced wrapping force (3-6 MPa of tensile strain produces an elongation of 10-30 %);
- 2) Easy tearing off by hand (capable of being easily pulled to the point of tearing without further elongation, and absence of whitening);
- 3) Suitable unwrapping force (tape peeling force vs. adhesive characteristic) of about 2 to 8 N for 19 mm width.

1.2.2 Thermochemical Targets

Chlorine-based products have flame-retardant and heat-resistant properties, and the replacement products must incorporate new techniques for flame-retardancy and heat resistance.

1.2.3 Electrical Targets

Since these products have been used in a wide variety of electrical applications the replacements should obviously have insulation performance equivalent or superior to that of PVC.

1.3 Materials Design

1.3.1 Tape Base Material

Since the base polymer for use in the tape must, first of all, have workability of the same level as PVC tape, it must exhibit stress-strain (tensile stress-to-elongation) characteristics close to those of the PVC product. Second is ease of tearing off by hand. This ease of tearing off is

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extremely important in materials design. These points were therefore taken into account in selecting the polymer, but while ethylene copolymers have properties comparatively close to those of PVC, tensile strength as single polymers is too high so that there are problems with both wrapping and tearing off properties. As flexible polymers, rubber-based materials are good, but used alone the tape itself lacks strength and thermal resistance, while elongation during tearing off is excessive. No single polymers can satisfy the required performance, so that blending techniques are needed, and it was decided to create a blend of rubber-based polymer combined with the increased strength and resistance of olefin polymer and

ethylene copolymer that exhibits tensile strength equivalent to PVC yet can reduce elongation. The three types of polymer blends had different physical properties depending on the composition and also behaved differently during tape manufacture, so a balanced composition was adopted.

Table 1 shows a comparison of the tape workability by the type of polymer used, and Figure 1 shows the stress-strain curves for PVC and halogen-free F-CO tapes in the range of the wrapping procedure. Photo 1 shows results for the ease of tearing off of the tape obtained during wrapping.

Next, to provide flame-retardancy, the composition of various flame-retardant agents was examined. Heeding environmental restrictions to be implemented in future, metal hydrates were incorporated, avoiding the use of phosphorus-based materials, and rubber-based polymers are suited to high levels of filling. Taking account of tape flexibility, high levels of filling are not possible and with the metal hydrate only flame-retardancy is insufficient, thus requiring the addition of an agent that enhances flame retardancy. By adding a flame retarding agent and a flame retardancy enhancer in suitable proportions to take account of flexibility it was possible to achieve a satisfactory level of flame retardancy--an oxygen index (OI) of 26. The metal hydrate was selected with regard to the temperature conditions of tape manufacture. Figure 2 shows the relationship between the amount of flame-retardant agent and the OI value.

A processing enhancer was also added to further improve the mixing characteristics, together with an aging preventive agent to improve the long-term performance.

A patent application has been filed for the tape described.

Table 1 Comparison of tape workability by type of polymer.

	PVC tape	Halogen-free tapes		Standard of workability
		Single-polymer	3-polymer blend	
Tensile strength N/10 mm	30	~10 or 50 - 100	20	10 - 40
Elongation (%)	310	600 or 150	490	250 - 600
Manual tearing off	◎	△	◎	Easily torn by hand
Whitening	◎	×	◎	Virtually unnoticeable

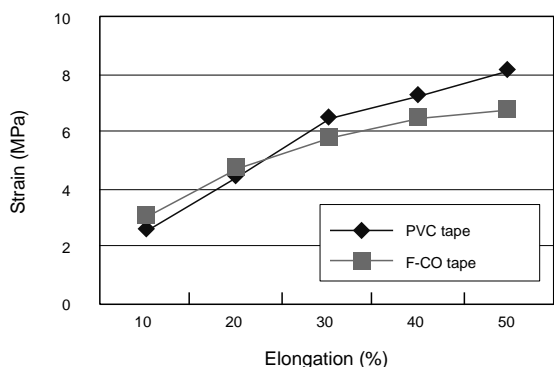


Figure 1 Stress-strain curves for PVC and halogen-free F-CO tapes.

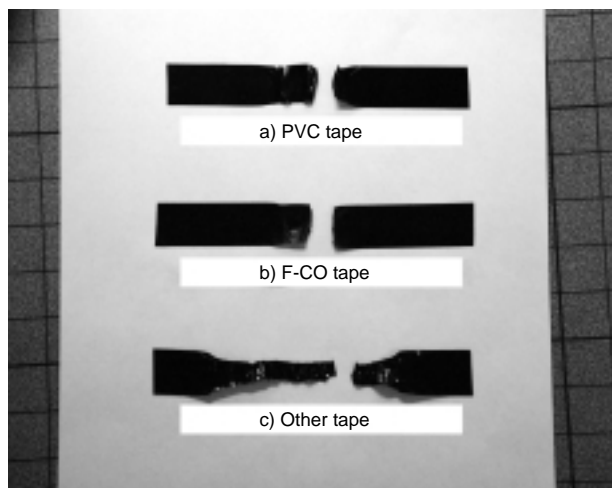


Photo 1 Tape parting results obtained during wrapping.

1.3.2 Tape adhesive

The tape requires an adhesive. Even if the adhesive layer is thin, there must be sufficient adhesive strength and unwrapping force (if the adhesive strength is too great, tape-wrapping characteristics will deteriorate.) With generally available acrylic adhesives or butyl rubber adhesives, the peeling force is weak (that is to say the tape unwrapping force is weak), so that the tape unwraps and tape-wrapping work is difficult to perform. And there is a problem of blocking (adhesive residue on the back surface of the tape) that prevents their plain use. As a solution to these problems we developed a proprietary composition consisting of an acrylic adhesive base with a suitable

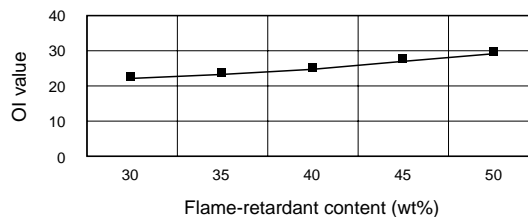


Figure 2 Relationship between amount of flame-retardant agent and OI value.

Table 2 Properties of non-halo F-CO tape.

Item	Unit	Non-halo F-CO	JIS C 2336 standard
Tensile strength	N/10 mm	20	15 or more
Elongation	%	490	100 or more
Adhesive force	N-10 mm	0.7	0.5 or more
Insulation breakdown strength	kV/mm	55	25 or more
Withstand voltage	kV for 1 min	5	5 or more
Volumetric resistivity	Ω -cm	2×10^{15}	2×10^{12} or more
Oxygen index (OI)	—	26	—

amount of a plasticizing agent.

Since field wrapping under winter conditions can involve temperatures near the freezing point, PVC tape becomes stiff and adhesive strength drops sharply. The tape developed in this work is better adapted to cold conditions, greatly increasing the workability at low temperatures.

1.4 Characteristics of "Non-Halo" F-CO Tape

In addition to the physical and thermochemical properties described above, the electrical properties of the halogen-free tape developed here were also satisfactory (see Table 2).

1.5 Summary

It has been possible to develop as a replacement for PVC tape a new type of fire-retardant tape that is halogen-free, does not use phosphorous and contains no lead compounds. In May 2001 it was announced in the press and was put on sale. In addition to the standard black color, it is also available in red, blue, white, yellow, brown and green, and is expected to be widely used in efforts toward environmental protection.

2. THERMALLY CONDUCTIVE SHEET "F-CO TM SHEET"

2.1 Introduction

As CPUs and other electronic computer components improve in performance, they generate more heat, so that effective cooling is an indispensable aspect of maintaining their performance. A commonly used method of accomplishing this is to channel the heat to a heat sink, but for the heat sink to conduct the heat properly a material having good thermal conductivity must be sandwiched into the intervening space. The performance of this included material is all-important.

2.2 Segmentation of the Market for Thermally Conductive Materials

Figure 3 shows the projected market for various thermally conductive products; significant growth is anticipated.

Thermally conductive materials may be categorized in two main forms--sheets and greases, but in recent times there have appeared intermediate materials such as gels

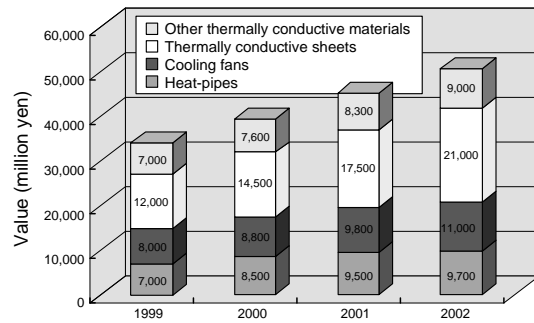


Figure 3 Projected market for thermally conductive products.

and phase-changing materials, which are solid sheets at normal temperature but change into grease as temperature rises.

2.3 Details of Materials Developed

From the physical attributes of flexibility and thermal conductivity, silicone rubber-based products are in overwhelming use. It has recently been found, however, that when the temperature of sheets of such materials rises, the low-molecular-weight siloxane they contain volatilizes into the equipment. It is then redeposited on the contact points of motors and relay switches and breaks down to form silicon dioxide, which acts as an insulator and contributes to point failure. This has created a strong demand for siloxane-free thermally conductive sheets that can be used with no loss of flexibility or thermal conductivity.

The F-CO TM sheets that have been developed and marketed by Furukawa Electric, though in the form of sheets, use an acrylic base polymer and, containing no silicone rubber, are free of LMW siloxane. They are also halogen free and offer a high degree of thermal conductivity.

For a polymer material, acrylic rubber itself exhibits a good level of thermal conductivity, but high-conductivity filling materials are added to improving performance, to a degree determined by the type and amount of filling material used.

Table 3 shows the thermal conductivity of several materials. Commonly used filling materials include aluminum oxide for ordinary applications, and high-cost boron nitride and aluminum nitride for products requiring high thermal conductivity.

F-CO TM sheets contain mainly magnesium oxide, which has higher thermal conductivity than the aluminum oxide used in general-purpose products. Magnesium oxide is highly water-absorbent, and when added to polymer in large amounts can cause stability problems. For this reason it has been avoided in the past, but new manufacturing techniques have made it possible to produce a product that is sufficiently hydrophobic as to be useful.

A number of patents have been applied for with respect to these thermally conductive sheets. Table 4 shows a comparison of the features of F-CO TM sheet with conventional silicone-based thermally conductive sheet produced by a competitor.

Table 3 Thermal conductivity (W/m•K) of selected materials.

Minerals	W/m•K	Fillers	W/m•K	Polymers	W/m•K
Diamond	2000	Boron nitride	210	Acrylic rubber	0.27
Silver	427	Aluminum nitride	170	Chloroprene rubber	0.25
Copper	398	Magnesium oxide	60	Silicone rubber	0.2
Gold	315	Aluminum oxide	36	Butyl rubber	0.1
Aluminum	237	Zinc oxide	25	Nylon 6	0.25
Magnesium	156	Carbon	10	Polyethylene	0.22
Iron	80			Polyvinyl chloride	0.16
SUS	15			Polystyrene	0.12

From the standpoint of resistance to heat and cold, the properties of the silicone rubber now in general use are outstanding. Considering the operating conditions of CPUs and other electronic components, however, such a level of thermal properties is unnecessary. And with silicone rubber it is impossible to reduce siloxane production to zero. We therefore decided to consider non-silicone rubber products, and developed and brought to market a material based on acrylic rubber, which was second only to silicone rubber in terms of heat resistance and had the highest thermal conductivity of all the polymers in Table 3.

With respect to applicability to the heat-generating portions of electronic equipment, the need for a siloxane-free material is urgent, and it has already been used in game machines, TV sets, laptop computers and audio equip-

ment.

The production of of F-CO TM thermally conductive sheets--mainly for game machines--now exceeds 2 million sheets per month. It is also under consideration for use in communications equipment, automotive electronics, hard disk drives and DVD equipment.

Table 5 shows its characteristics.

2.4 Conclusion

F-CO TM sheets were brought to market in August 2001 and large numbers of inquiries have been received. Currently available, in addition to the products already mentioned, are:

- 1) Thermally conductive sheets to enhance the effect of preventing electromagnetic interference (EMI).
- 2) Thermally conductive sheets with strong adhesion on both surfaces;
- 3) Low-rigidity thermally conductive sheets for applications requiring flexibility.

All of these sheets are halogen-free, and have flame-retardant properties.

With the increasing need for electrical, electronic, communications and automotive equipment to be more compact, more functional, and more resistant to EMI noise, these products are expected to contribute to the expansion of IT-related fields.

Table 4 Comparison of features of F-CO TM sheet with competitor's product.

Property	F-CO TM	Competitor
Base material	Acrylic rubber	Silicone rubber
Heat withstand temp.	Approx. 180°C	Approx. 220°C
Cold withstand	Approx. -40°C	Approx. -60°C
Thermal characteristics	Good	Good
Siloxane produced	No	Yes
Cost effectiveness	Excellent	Good

Table 5 Characteristics of F-CO TM sheet .

Description	Standard	Single-layer adhesion	High thermal conductivity	Insulating		Thin film		
				Single-sided adhesion	Two-sided adhesion	Al-foil center layer, two-sided adhesion		
Type	2014	N-500	EE	EN500/50-1	EN500/50-2	A90/20-2	A250/100-2	
Standard dimensions	T (mm)	1	0.5	1	0.5	0.5	0.09	0.25
	W (mm)	210	190	115	200	200	240	240
	L (m)	10	0.19	25	0.4	0.4	100	100
Thermal conductivity (W/m•K)	1.6	1.6	2.5	1.6	1.6	1.4	1.4	
Thermal resistance (°C/W)	0.57	0.31	0.5	0.35	0.28	0.13	0.31	
Volumetric resistivity (Ω-cm)	1X10 ¹²	2.7X10 ¹²	1X10 ¹²	2.5X10 ¹¹	3.9X10 ¹¹	—	—	
Insulation breakdown voltage (kV/mm)	20	28	20	35	33	—	—	
Adhesive force to Al (N/25 mm)	—	3.6	—	2.8	3	1.5	6.5	
Flame-retardancy (by UL94)	V-0 equivalent	—	V-0	HB	HB	—	—	
30 % compression strength (N/cm ²)	84	27	80	130	100	—	—	