ThreeBond
TECHNICAL NEWS

Three Bond Technical News
Issued July 1, 2002

59

Sealants for Lithium-Ion Batteries

Introduction

As portable electronic devices become increasingly compact, their parts must be made ever smaller. In addition, there is increasing demand for technological innovations in batteries for such devices; for example, a small, long lasting battery is a requisite for cellular phones. To increase the performance of batteries under such circumstances, improvement in the sealants used in their assembly is expected.

This issue introduces the battery market and discusses the development of battery sealants that can be expected to flourish in the market.

Contents

1. Brief Description of Lithium-Ion Batteries

Various batteries are now on the market, and are broadly classified into two types: chemical batteries and physical batteries. Chemical batteries utilize chemical reactions (electrolytic reactions) to generate electricity, while physical batteries induce cell reaction in response to specific external stimulation (with solar batteries being a representative example). Lithium-ion batteries are classified as chemical batteries and feature the highest power among those currently available batteries, and their capacity increases year after year.

A battery generates electricity by transporting electrons between electrodes. In a lithium-ion battery, the positive electrode is made of carbon and the negative electrode is made of lithium. Battery manufacturers have extensive know-how with respect to the crystalline structure of carbon used as the material of the positive electrode. The most significant difference between lithium-ion and other batteries is that the former uses organic solvent as its electrolytic solution. This is due to the fact that the electrolyte is easily dissolved into the organic solvent during the electrolytic reaction. As this electrolyte is very sensitive to water, it is made of non-aqueous material. The reason for it being very sensitive to water is as follows:

From the position of Lithium in the periodic table, i.e., just below hydrogen, it is understood that Lithium belongs to the same group as the elements that constitute water, which means that it has a high affinity with water. It is for this reason that Lithium-ion batteries are considered water-sensitive.

Shown below are the materials that compose lithium-ion batteries.

- Electrode
  - Positive electrode: Carbon + binder resin
  - Negative electrode: Lithium compound + binder resin
- Electrolytic solution
  - Organic solution
- Electrolyte
  - Halogenated lithium salt
- Separator
  - Nonwoven fabric

It is clear from the components listed above that the lithium-ion battery is an aggregation of organic compounds. The components of the lithium-ion battery are different significantly among its types and manufacturers. For example, the composition of electrodes and electrolytes differs between primary and secondary batteries. In addition, individual battery manufacturers employ unique combinations of materials to configure a battery. Each manufacturer pursues unique battery designs with the goal of creating batteries with more power than any that have come before them.

We believe that electrolytic solution and electrolyte are vital materials of lithium-ion batteries, and that finding the optimum combination of the two materials is a key point in developing high performance batteries. It is not an exaggeration to say that the combination of electrolytic solution and electrolyte determines the performance of lithium-ion batteries. As the safety and recyclability of batteries have been the focus of a great deal of attention in recent years, the minimization of environmental load of the electrolytic solution and the dehalogenation of the electrolyte have become important issues. However, there has always been the inherent contradiction that the solution of these issues represents an obstacle to the creation of high power batteries. The battery manufacturing industry is making efforts to resolve this contradiction.

2. Primary and Secondary Batteries

In the industry, there are various technical terms with respect to batteries, including lithium-ion batteries. Such terms are summarized herein.

Batteries are broadly classified into two categories: primary batteries and secondary batteries. However, with the introduction of solar batteries and fuel cells, batteries have recently begun to be categorized as either chemical or physical batteries. Primary batteries are so-called "disposable batteries" that can be used only once. Dry batteries are typical primary batteries, and a recycling campaign for disposable batteries has recently been actively organized. Cylindrical and square shapes are the most popular. The button batteries used in cameras and portable game machines are typically shaped primary batteries. Secondary batteries are rechargeable batteries. As secondary batteries are used primarily as a power source for specialized equipment (in the form of a battery pack), unlike primary batteries, they are generically referred to as "batteries." The word makes most people think of storage batteries. Storage batteries are rechargeable and are thus classified as secondary batteries as well. Fuel cells have attracted considerable attention as next-generation batteries. As the designs of fuel cells differ completely from those of the batteries discussed above, primary and secondary batteries are not an appropriate categorization approach for fuel cells. Fuel cells are secondary batteries in a broad sense but, taking into consideration their designs and applications, it can be said that fuel cells are an energy system.

3. Energy Density of Lithium-Ion Batteries

Among batteries for which there is increasing demand that they be made "lighter, thinner, and smaller," the greatest demand is placed on lithium-ion batteries due to their excellent capabilities, particularly their high energy density. Nickel metal hydride (NiMH) and lithium-ion batteries feature the highest performance among batteries currently on the market. While the former are popularly thought of as "clean" batteries, their shapes are limited and many difficult technologies are required to make them compact and lightweight in design. On the other hand, the latter utilizes ions to induce electrolytic reaction, making it is possible to generate electricity as long as there is sufficient space to allow ionic conduction. Fig. 1 compares the battery potentials (i.e., energy densities) necessary for the generation of electricity. The per-weight energy density of the NiMH battery is as high as 100 Wh/kg due to the fact that a metallic material is used as the main power-generating component. The per-weight energy density of the lithium-ion battery shows the highest value, at 150 Wh/kg. As the energy density can be directly converted into energy efficiency, it can be said that a higher energy density will result in greater electromotive force, i.e., increased power. The current target energy densities of lithium-ion secondary batteries are 300 Wh/L (per-volume energy density) and 150 Wh/kg (per-weight energy density). Now, even inorganic and polymer batteries, both of which have heretofore not been considered R&D items, in addition to new hybrid batteries, are under study using these figures as development goals. Fig. 2 shows trends in the overall weights of portable electronic devices on a year-by-year basis. It can be seen that the overall weights of portable electronic devices have remained at nearly the same level, despite the fact that their performance has improved steadily. It is estimated that lightweight batteries, together with lightweight peripheral parts, contribute to the constant device weights.

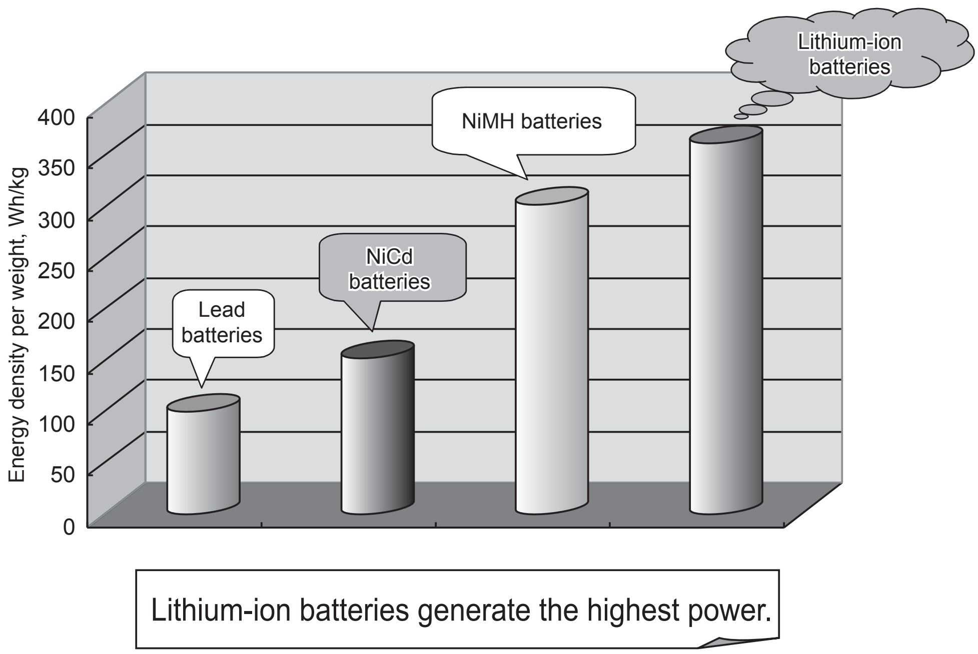

Fig. 1 Comparison - Energy Densities of Secondary Batteries

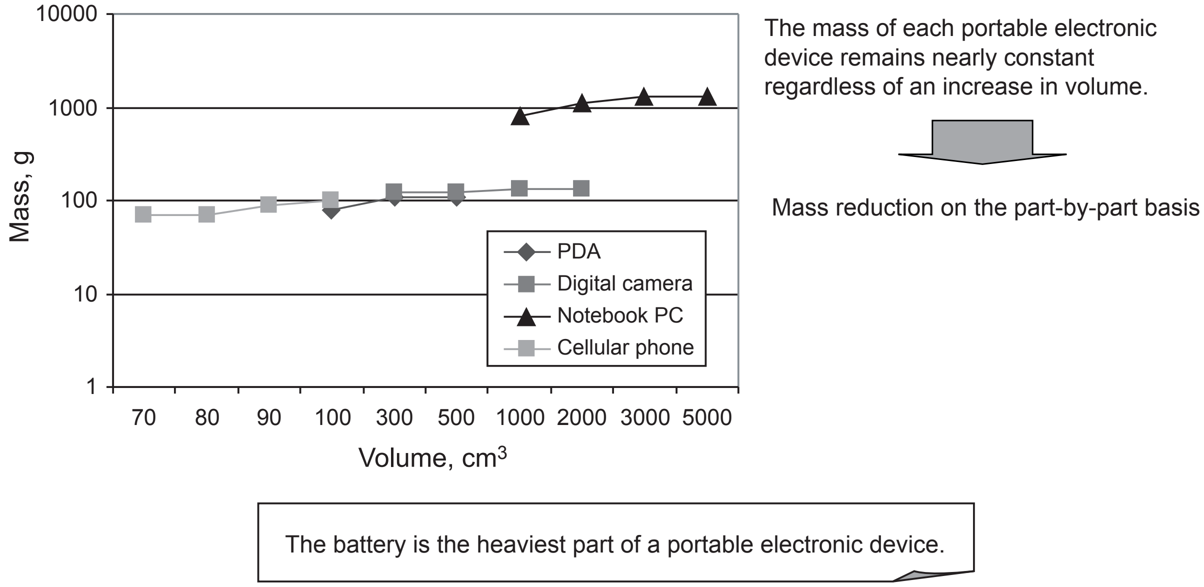

Fig. 2 Volume vs. Weight - Portable Electronic Devices (Survey in FY2000)

4. Introduction of Three Bond's Sealants

Due to its unique structure, each lithium-ion battery consists of various materials. As lithium-ion batteries are being developed continuously, battery manufacturers are setting the highest development goals and working to develop extremely high power and high efficiency batteries. The components of lithium-ion battery have been briefly explained in previous sections; this section primarily discusses the future prospects for and Three Bond's contributions to the development of lithium-ion batteries.

4-1 Introduction of Lithium-Ion Battery Sealants, ThreeBond 1170B and 1171

ThreeBond (hereinafter referred to as "TB") 1170B and 1171 are sealants developed for lithium-ion batteries (see Table 1). Their major component is olefin hydrocarbon. As the polymeric principal chain structure of this olefin hydrocarbon is neutral, each sealant strongly withstands electrolytic solution. Previously caulked sections and packing entrances, where sealing is required, are sealed with asphalt pitch or other materials. The problem has been pointed out that since the asphalt contains chains composed of relatively low molecules, areas adjacent to or exposed to the electrolytic solution suffer from decreased sealing performance. With the recent trend toward "lighter, thinner, and smaller" and high power batteries, battery manufacturers are forced to reduce the sealing area. For this reason, they are making every effort to continue using the asphalt pitch by improving the battery design. Due to their excellent sealing performance, TB1170B and TB1171 allow to seal batteries satisfactorily without changes to the structural design of a battery. In addition, we believe that higher sealing performance can reduce the sealing area without reducing the battery capacity.

Table 1 Properties of Lithium-Ion Battery Sealants

	TB1170B	TB1171	Test method	Remarks
Appearance	Colorless	Colorless	3TS-201-01	Visual
Viscosity, mPa•s	2400	400	3TS-210-01 or -02	BL/BH rotational viscometer
Specific gravity	0.87	0.87	3TS-213-02	Specific-gravity cup method
Nonvolatile content, %	15	4.5	3TS-217-01	Weight-change ratio after heating at 160°C

Fig. 3 compares TB1170B, TB1171, and asphalt pitch with respect to their resistance against electrolytic solution. General electrolytic solutions, dimethoxy ether (DME), propylene carbonate (PC), and ϒ-butyrolactone (ϒ-BL) were used in this test. Our sealants are designed to offer a higher molecular weight and smaller amount of low molecules compared to the asphalt pitch. As a result, our sealants have less component elution from high polarity electrolytic solutions compared to pitches. This fact can be clearly seen in the test result shown in Fig. 3. It has been proven that our sealants have higher electrolytic-solution resistance than asphalt pitch, and that components are not eluted into electrolytic solutions even under high temperature conditions.

Fig. 4 shows a comparison of permeability tested under various conditions. It is clear from this figure that TB1171 has the lowest permeability among the test materials, and that this characteristic is substantially improved compared to the asphalt pitch. This is the result of the unique molecular structure of TB1171 and TB1170B, i.e., their neutral chain structure and low permeability design, as previously discussed.

Fig. 5 compares the thermal viscoelasticities of TB1171 and asphalt pitch. Many sealants now feature solder reflow resistance in response to market needs; therefore, we measured the storage elastic modulus under heat as one of the features of these sealants. It was proven that when stress was gradually applied to the asphalt pitch at 260°C, its storage elastic modulus dropped at low stress levels. On the other hand, the storage elastic modulus of TB1171 did not fall at the test temperature. This test result shows that TB1171 is not destroyed by the stress accumulated in the battery (i.e., the pressure increase due to the evaporation of electrolytic solution) even under high temperature conditions, and that the resin maintains its elasticity even after the stress increase.

Test method and conditions:
Apply 0.1 g of each resin to a glass plate so that the coated area will be 15 mm across and 100 μm in thickness. Immerse the coated glass plate in the specified electrolytic solution for 10 days at 60°C, and calculate the weight-change ratio using the weights measured before and after the test.

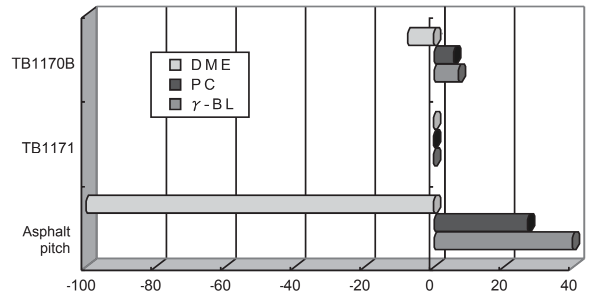

Fig. 3 Comparison of Three Bond Battery Sealants and Asphalt Pitch

Test method and conditions:
In accordance with JIS K7129 "Test method for the water-vapor transmission rate of plastic film and sheeting," measure the permeability of resin 100 μm in thickness.

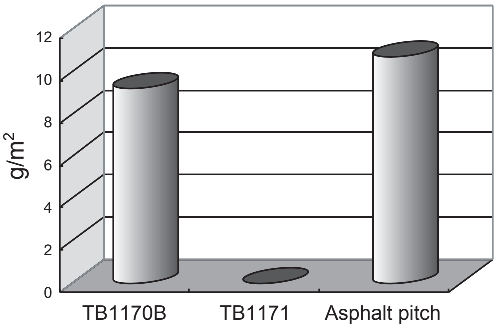

Fig. 4 Comparison of Sealants - Permeability

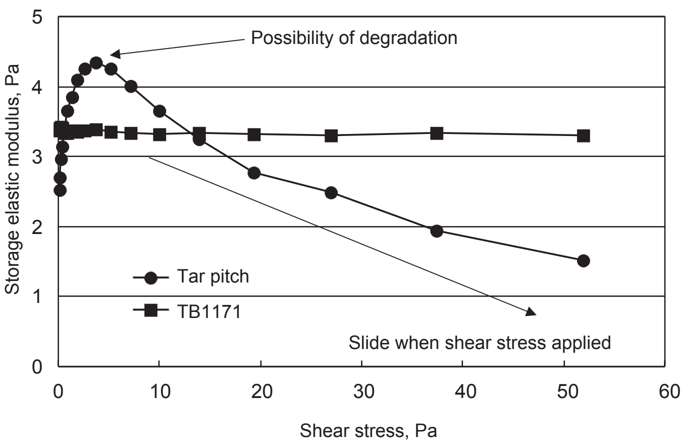

Fig. 5 Comparison of Sealants - Thermal Elastic Modulus (Heating Temperature: 260°C; Frequency: 1 Hz)

4-2 Introduction of the Battery-Pack Sealant ThreeBond 1530D

Recently, many home electric appliances are being made smaller and lighter. As a result, batteries are frequently used as the power source of these devices, including a slew of lithium-ion secondary batteries, due to their large energy density. Despite this trend, the leakage of electrolytic solution has been a serious problem, and the industry is making every effort to develop technologies that will contribute to the secondary prevention of leakage. Specifically, battery packs used in portable PCs are being designed taking into consideration the possibility that surrounding electrodes, printed circuits, and electronic parts will be damaged by the electrolytic solution (or electrolyte) leaking from battery packs. The most popular technique for protecting printed boards and the like is to coat and seal these electronic parts and battery packs with resins.

Moisture-curing silicone resin is a conventional material widely used as a coating sealant, but this resin is dissolved into electrolytic solutions, losing the expected coating and sealing effect as a result. In addition, as a thin coat of the resin cannot withstand electrolytic solutions, it is expected that it will be necessary to apply a thick coating of the resin. However, such a thick application will increase the weight of the battery, contrary to the current needs. Even if silicone resin is used, the structural design of the battery pack will be greatly restricted and, for this reason, the material cannot be used as a permanent measure. If the electrolytic solution leaked inside the battery pack and the sealant could not be dissolved into the electrolytic solution or swelled, the solution would remain in the battery pack, which would have negative environmental effects. When a hard resin is used, it may come off from the battery during the drop test, for example. If the resin comes off from the tab or other parts after curing, the electrolytic solution will pass through the partition wall with the aid of capillarity to corrode the electric circuit.

To solve this problem, Three Bond has developed a moisture-curing elastic sealant, TB1530D, which is designed for use in battery packs. The major component of the resin used in TB1530D is a special polymer that contains a silyl group and cures as a result of reaction with a small amount of moisture in the air. TB1530D offers excellent adhesion and bonding capabilities for a wide variety of materials, including metals, plastics, rubbers, and inorganic materials, and features low viscosity. Therefore, this sealant is suitable for coating applications. Table 2 lists the properties and characteristics of TB1530D.

Table 2 Properties and Characteristics of TB1530D

		Appearance	Unit	Measurement results	Remarks
Properties	Appearance	3TS-201-02	-	Gray	
	Viscosity (25°C)	3TS-210-02	Pa•s	20	BH, No.6, 20 rpm
	Specific gravity (25°C)	3TS-213-02	-	1.39	
	Dry-to-touch time	3TS-219-05	min	5	
Characteristics	Curing conditions: 25°C, 55 %RH, 7 days				
	Hardness	3TS-215-01	-	A34	
	Peeling property	3TS-320-01	MPa	3.2	No. 5 dumbbell
	Elongation	3TS-320-01	%	220	No. 5 dumbbell
	Peeling shear adhesive strength	3TS-301-13	MPa	2.5	

As the cured TB1530D, unlike those of the aforementioned TB1170B and TB1171, is swelled by the electrolytic solution in a lithium-ion battery, the electrolytic solution is gelled to lose fluidity, and consequently the electric circuit is protected from contact with electrolytic solution. As TB1530D is also an elastic material, it will not be separated from the battery parts even when the battery pack is dropped onto a hard object. This contributes to increasing product safety.

The leakage prevention system for lithium-ion batteries is illustrated in Fig. 6. TB1530D should be coated on the electrodes to which the control circuit and battery units are connected, and on those portions from which it is most likely that the electrolytic solution will leak. If the electrolytic solution leaks, the cured TB1530D will absorb the solution to prevent flowing out. The cured TB1530D swells with electrolytic solution, and, by adhering the resin with the electrodes, protects electrolytic solution to penetrate into electric circuits with capillarity. Fig. 7 shows an example of a battery pack.

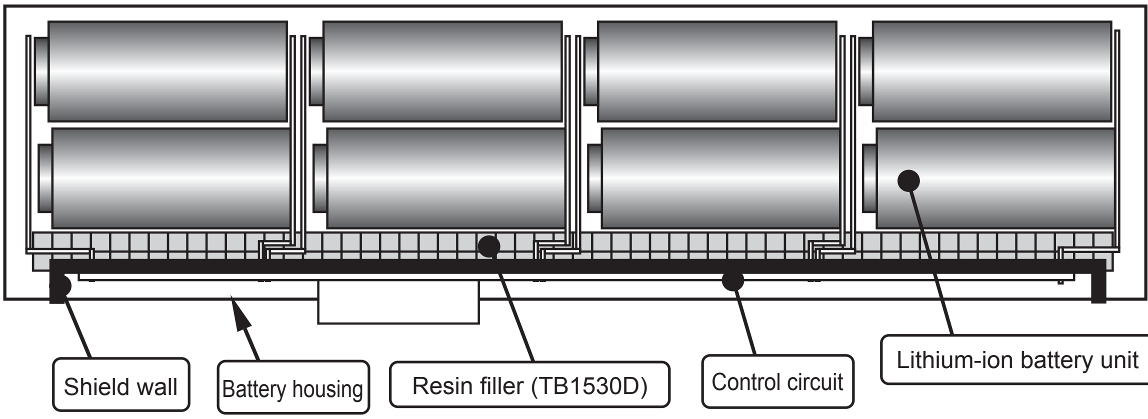

Fig. 6 Lithium-Ion Battery Leakage Prevention System

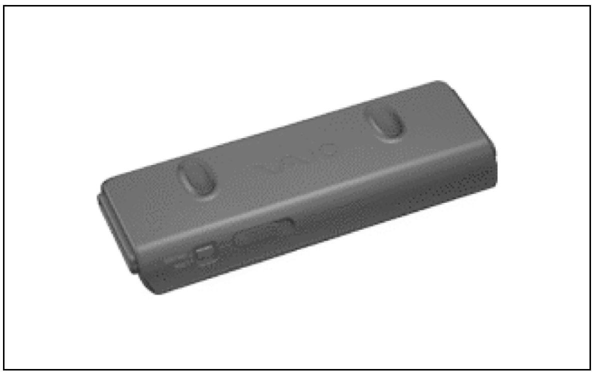

Fig. 7 Battery Pack (photograph provided by Sony Corporation)

5. Conclusion

Various resin materials are used in order to compose of batteries, and it is no exaggeration to say that individuals are key materials to improve performance of batteries. It is forecasted that the trend toward "lighter, thinner, and smaller" for portable electronic devices will be continued and heated. We are studying various plans to develop not only sealants but other resins as well. We hope you continue to have interests on this trend and watch closely our activities in the future.

Katsuhiko Kishi
Research Section
Research Department
Ho Kenkyo
Material Development Section
Development Department

Research Laboratory
Three Bond Co., Ltd.

ThreeBond
TECHNICAL NEWS
THREE BOND CO., LTD.
1456 Hazama-cho, Hachioji-shi, Tokyo 193-8533, Japan
Tel: 81-426-61-1333