Progress in polyethylene separators for lead–acid batteries

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Abstract

The types and properties of separators used for lead–acid batteries are reviewed. Attention is focused on the pocket-type polyethylene (PE) separator as this is widely used in present-day automotive batteries, i.e. in low-maintenance batteries with expanded lead–calcium grids. An improved PE separator has been developed by using a PE resin of high molecular weight. The resistance of the separator to attack by hot sulphuric acid is increased by a factor of 1.5. Batteries using the improved separator show a 40% increase in lifetime under the SAE 75 °C life-cycle test. © 2002 Published by Elsevier Science B.V.

Keywords: Automotive battery; Lead–acid; Molecular weight; Oxidation resistance; Polyethylene separator; Resin

1. Introduction

The environment of the automotive battery has been increasing in severity in recent years. As the electronics in the total vehicle system improve, the requirement for increasing the reliability of the automotive battery is more urgent than before. Moreover, the ambient temperature of the automotive battery shows a tendency to become higher because of the high power, the closely-packed engine components, and the increase in traffic congestion in cities. In addition, the market demand for reduction in battery maintenance, such as water addition which the user has to carry out, is becoming more intense.

Given these issues, the automotive battery has changed from a conventional low-antimony-type to a hybrid-type and, finally, to a calcium-type. Consequently, a sophisticated and low-maintenance battery (this is abbreviated as 'MF battery' in the following) has been developed, and it meets the requirements of the market.

The improvement and development of the separator discussed in this paper proceeded in accordance with the changes in the specifications for the batteries which were first made with wooden separators, then progressed through microporous rubber separators, cellulose separators and synthetic pulp separators with glass mats (hereafter, abbreviated as the SPG separator), and now polyethylene separators (hereafter termed the PE separator) have evolved. This sequential change in separator technology has provided continuous improvements in the charge and discharge efficiency of batteries and has given high vehicle-starting capability and reliability. Moreover, short-circuits (caused by particles of active material dislodged from the battery plates) are prevented due to the smaller pores and excellent electrochemical oxidation resistance of the PE separator. These features also contribute greatly to the improvement in battery life.

2. Progress in lead–acid automotive batteries and their separators in Japan

The types and features of automotive lead–acid batteries are shown in Table 1. The specifications for the battery have been modified in accordance with the trend towards MF batteries. For example, the grid alloy has been changed progressively from an antimony alloy to a low-antimony alloy, to a hybrid and, presently, to a calcium alloy in order to reduce water losses during charging. The grid-manufacturing process for calcium alloys has also been changed from the conventional casting method to the expanding method. With expanded grids, the positive active-material can fall out more readily than with the cast-type. Thus, a pocket-type separator is required (Fig. 1).

Typical separators used for lead–acid batteries throughout the world are listed in Table 2, together with the battery characteristics. Among these, the leaf-type SPG separator and the pocket-type PE separator are used in Japan according to the battery application, battery usage, and system requirements. The SPG separator is used together with a

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Table 1
Types and features of automotive lead–acid batteries

Item	Calcium MF battery	Hybrid MF battery	Low-antimony MF battery	Conventional battery
Composition of electrode (positive/negative)	Ca/Ca	L–Sb/Ca	L–Sb/L–Sb	Sb/Sb
Manufacturing method of grid	Expanded	Cast/expanded	Cast	Cast
MF property	Better	Good	Not good	–
Separator	Pocket-type	Pocket-type	Leaf-type	Leaf-type
Productivity	For mass production of small kinds	For mass production of small kinds	For production of many kinds	For production of many kinds

glass mat in heavy-duty batteries that must have high vibration and temperature durability in vehicles such as buses, trucks and taxis that operate under severe conditions. The PE separator is generally employed in batteries for passenger cars with a light load and is used in about 70% of these batteries. Regarding the background in which the PE separator is widely used: (i) the road conditions in Japan have been improved so that battery vibration during driving has decreased and, accordingly, the requirements for vibration resistance have been reduced; (ii) because the grid has been changed from a conventional cast-type to an expanded-type (calcium alloy) due to popularisation of the MF battery,
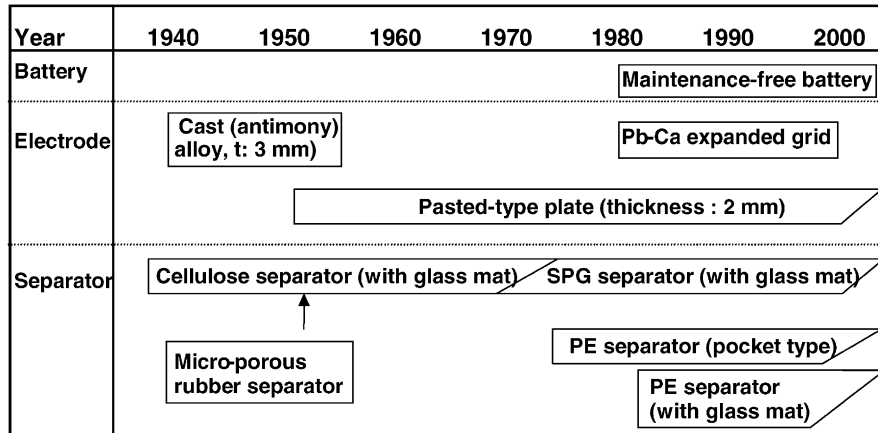

Fig. 1. Progress in automotive lead–acid battery technology in Japan.

Table 2
Types of separator and battery characteristics

Item	Pocket-type			Leaf-type	
	PE separator	PE separator (with glass mat)	SPG separator (with glass mat)	Cellulose separator	Sintered PVC separator
Battery characteristics					
Excellent starting capability	Better	Not good	Good	Good	Good
Vibration durability	Not good	Better	Better	Not good	Not good
High temperature durability	Not good	Better	Better	Not good	Good
Main use	Passenger cars	Buses, trucks, etc.	Four-wheel cars Motorcycles	Passenger cars Motorcycles	Passenger cars Motorcycles
	Light-load use	Heavy-load use	Light-heavy-load use	Light-load use	Light-load use
System requirements	Cold to clement regions (for good road conditions)	Cold to clement regions (for good road conditions)	Clement to tropical regions (can be used satisfactorily even under bad rod)	Clement to tropical regions (can be used satisfactorily even under bad rod)	Clement to tropical regions (can be used satisfactorily even under bad rod)
Effects of road condition					
Productivity of battery	High for mass production	Low because of applying the glass mat	Low for small production lots	Low for small production lots	Low for small production lots

a separator capable of being shaped into a pocket is needed to prevent loss of active material from the positive plate; (iii) the change from the leaf-type to the pocket-type separator has contributed considerably to an increase in productivity of battery manufacture; (iv) the durability of the PE separator has been greatly improved since its introduction to the market (around 1980), present versions do not crack easily and meet the requirements of high ambient temperature operation of the battery.

3. Function and properties of separators

Though the separator does not take part directly in the electrochemical reactions of the lead–acid battery, it is an indispensable component. The main functions and properties of the separator are as follows:

- to isolate the positive and negative plates both mechanically and electrically and, thereby, to prevent the formation of short-circuits;
- to prevent the passage of particulate material while allowing free passage of ions with low electrical resistance;
- to allow excellent diffusion of the electrolyte with minimum displacement of electrolyte;
- good chemical stability in the presence of sulphuric acid;
- high resistance to oxidation over a wide temperature range;
- high purity.

The properties of typical separators are shown in Table 3. The separators used in Japan are the PE and the SPG varieties. Both these separators have low electrical resistance and a small average pore size.

3.1. Electrical resistance

Electrical resistance influences the engine-starting capability of the battery. A separator with low electrical resistance is used particularly in cold areas to prevent a decrease in the electrical discharge output of the battery. The SPG and the PE separators are suitable for such purpose.

3.2. Average pore size

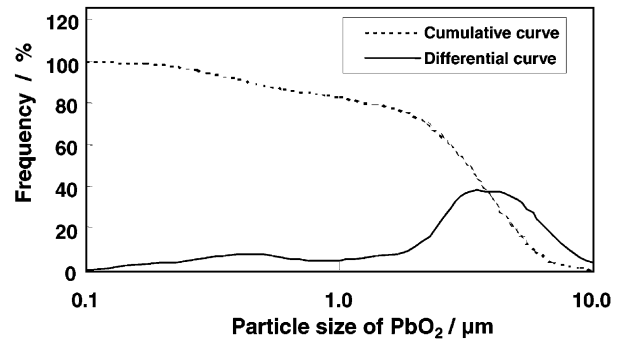The average pore size of the separator is an important property for mechanically isolating the positive and negative

Fig. 2. Particle-size distribution of PbO_2 particles.

plates. With charge–discharge cycling, the positive active-material can 'soften' and can fall out of the plate. One of the purposes of the separator is to prevent short-circuits due to dislodged particles. The following testing was performed to determine the pore size of the separator required to isolate such particles.

Particulates of lead dioxide were made from two pure-lead plates by applying electrolysis for 48 h (current density, $0.2 \ A/cm^2$) in sulphuric acid of 1.300 relative density at 50 °C. The particle-size distribution was measured and is shown in Fig. 2. It is seen that 80% of the particles are 1–10 μm in diameter. It is assumed that the particles produced by electrolysis of pure-lead plates have the same particle-size distribution as shed active material in a battery. Filtration tests of various separators were conducted in sulphuric acid solutions which contained these particles.

The results are shown in Fig. 3. The particles are scavenged by the PE separator and the synthetic pulp (SP) separator which have small pore sizes, and the filtrate is transparent. By contrast, the particles pass easily through the cellulose and sintered PVC separators, because their pore sizes are large, and the colour of the filtrate is brown.

The pore-size distribution of various separators is given in Fig. 4. The data provide the following observations.

- Because both the cellulose and the PVC separators have a pore-size distribution between 5 and 100 μm, their isolation capability for shed particles is poor.
- The SP separator is effective for the isolation of shed particles because 60% of the pore volume consists of pores of <1 μm in size.

Table 3
Separators for lead–acid batteries

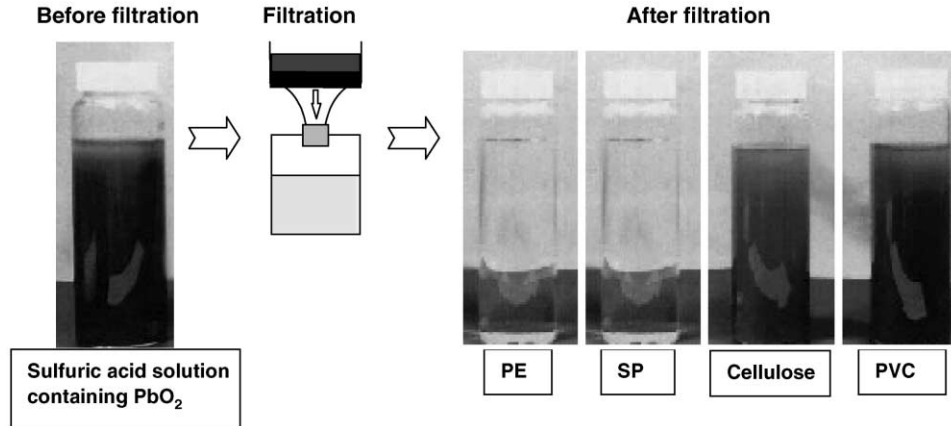| Item	PE separator (pocket-type)	SPG separator (leaf-type)	PVC separator (leaf-type)	Cellulose separator (leaf-type)
Total thickness (mm)	1.00	1.00	1.00	1.00
Backweb thickness (mm)	0.25	0.30	0.40	0.60
Glassmat thickness (mm)	–	0.70	–	–
Electrical resistance ($\Omega \times 100 \ cm^2$ per PC)	0.0009	0.0007	0.0016	0.0018
Average pore size (μm)	0.1	2	15	25

Fig. 3. Colour of sulphuric acid after filtration with various separators.
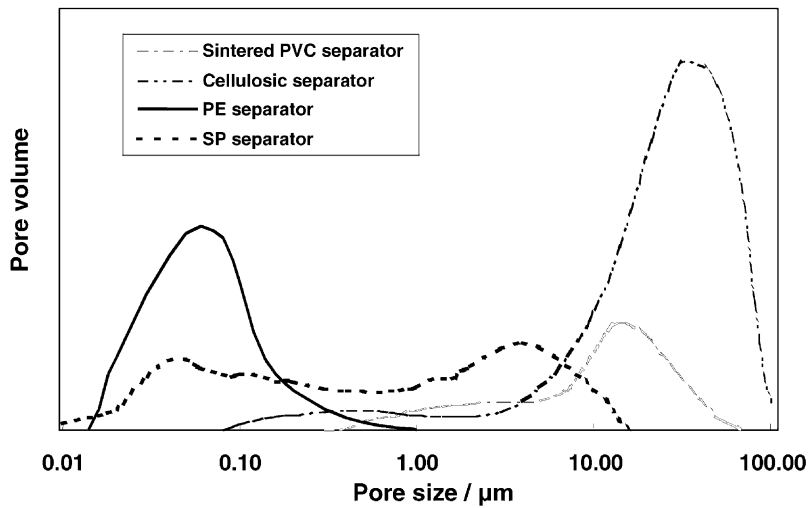

Fig. 4. Pore-size distributions of various separators.

• The PE separator excels in the isolation of shed particles because its pore size is very small (<1 μm).

4. PE separator

4.1. Current status of PE separator

The PE separator is manufactured by mixing polyethylene resin, silica powder, and oil. The mixture is then extruded. Afterwards, small pores are formed in the separator by extracting the oil. Therefore, excellent battery characteristics of low electrical resistance and short-circuit prevention are obtained when using PE separators.

The separator is not only exposed to the battery electrolyte, which is a strong acid, but is also attacked by the oxidation and reduction reactions due to the electrical charge and discharge reactions. This represents severe conditions for the PE separator which is an organic material.

In recent years, the backweb of the PE separator has become thin (it has decreased from 0.25 to 0.20 mm in

Japan), and failure attributed to the separator is becoming a problem.

There are two types of short-circuits attributed to the PE separator, as shown in Fig. 5. The short-circuit between the electrodes is due to a crack, while that between the electrodes is due to the formation of a hole which is caused by oxidation of the separator. The frequency of short-circuits as a result of cracks is high.

Finally, the engine compartment has become smaller and the ambient temperature of the battery has risen so that a separator which can withstand high temperatures is required.

4.2. Deterioration of PE separator

The PE separator of the lead–acid battery can be decomposed to peroxides when exposed to nascent oxygen, or when it comes into contact with the positive active-material. This deterioration becomes worse under high-temperature conditions.
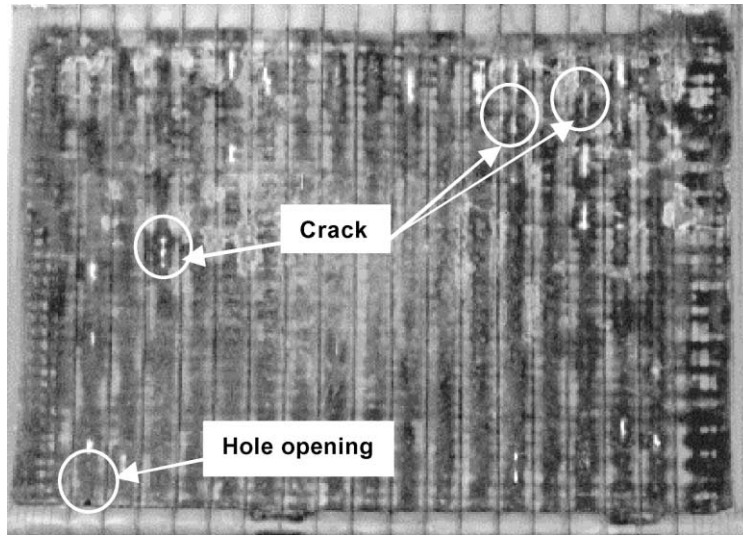
Fig. 5. Status of oxidation deterioration of PE separator.
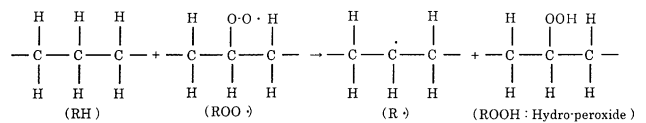
4.2.1. Oxidation

The positive active-material gradually degrades into min-ute particles during charge–discharge cycling. The active material is alternately converted to lead oxide (charging) and lead sulphate (discharging), and eventually softening occurs and the active material easily falls out of the grid. The dislodged active material retains its activity until it changes to lead sulphate on contact with sulphuric acid. Therefore, oxidation of the shed particles proceeds in the proximity of the positive plate. In this oxidative atmosphere, the –C–H– structure of the main separator material reaches an unstable state, and the –H– in the organic substance is removed by the –O– due to a strong affinity between –O– (oxygen) and –H– (hydrogen). The organic substance then decomposes, and finally it becomes water and carbon dioxide. The process is shown schematically in Fig. 6.

The oxidation mechanism of the PE resin involves:
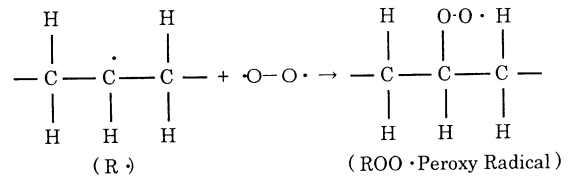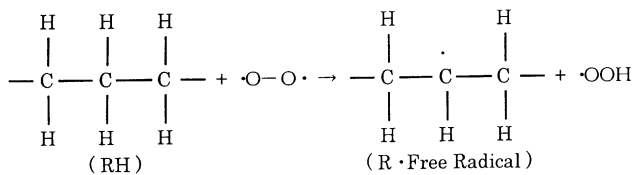
- A generated radical further reacts with oxygen and becomes a peroxy radical.
- The peroxy radical reacts with the polymer (RH) and forms hydroperoxide and a radical.

The hydroperoxide is formed as described above, and an auto-oxidation reaction starts. The hydroperoxide decom-poses into an alkoxy radical (RO$^\bullet$) and an hydroxy radical ($^\bullet$OH).

The alkoxy radical and the hydroxy radical form radicals which attack the polymer. Thus, a chain reaction takes place.
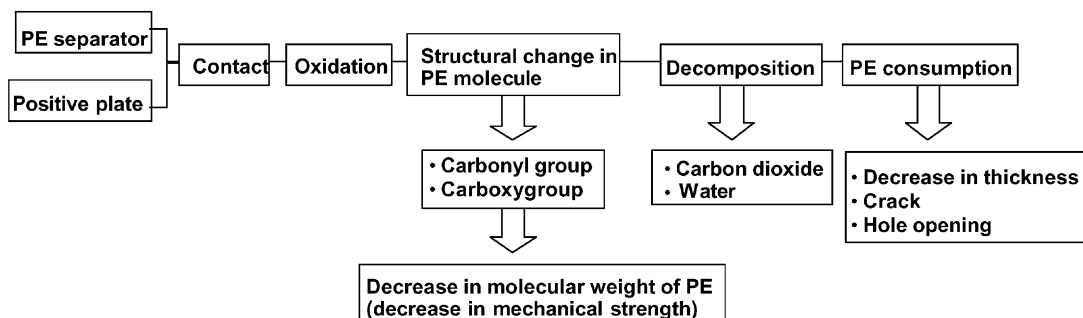

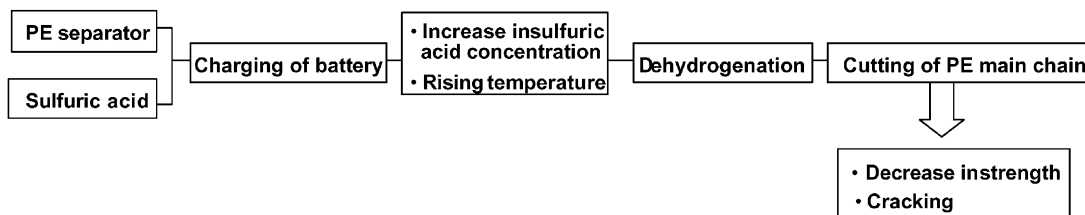Fig. 6. Process of deterioration of PE separator (oxidation consumption).

Fig. 7. Process of deterioration of PE separator (cracking).

The hydroperoxide formed in this reaction reacts further and is finally consumed to produce water and carbon dioxide.

4.2.2. Cracks

The electrolyte consists of sulphuric acid and pure water, though it often contains impurities and additives. The electrolyte loses water due to evaporation and electrolysis at the end of charging. The degree of water loss increases with rise in temperature. Under these conditions, the PE resin is broken in the main chain of the PE molecule by a dehydrogenation reaction with the concentrated acid. Consequently, the mechanical strength decreases and cracking occurs in the PE separator. The process is shown schematically in Fig. 7.

5. Improving electrochemical oxidation resistance of PE separators

Typical methods for improving the electrochemical oxidation resistance of PE separators are listed in Table 4.

5.1. Molecular weight of PE resin

The PE resin has excellent chemical durability because it has a straight-chain structure, i.e. $(-CH_2-CH_2-CH_2-)_n$, and few side chains or radicals that can cause deterioration. The general properties of the PE resin are listed in Table 5. The resin used for the PE separator has a mean molecular weight of 1,000,000 or more, and it is called a super-polymer PE.

In order to improve the electrochemical oxidation resistance of the separator, a super-polymer PE resin with a still larger molecular weight than that of the PE resin is now being used, as shown in Fig. 8. Nevertheless, the use of a PE resin with a high molecular weight leads to a decrease in workability in the forming (extruding) process and this conflicts with the improvement in the separator properties. Selection of a resin which provides the required separator properties and workability is, therefore, necessary. Accordingly, separators of mixed composition are under examination.

The relation between the molecular weight and the electrochemical oxidation resistance (electrochemical oxidation time, resistance to hot sulphuric acid), which has an effect on the lifetime of the separator, has been examined. A PE resin with a molecular weight 0.5–1.6 times that of the standard resin material has been used. The results are shown in Table 6.

The sample (70 mm × 70 mm) was set so that the rib faced a lead plate (50 mm × 50 mm) which was placed on it

Table 4
Methods for improving electrochemical oxidation resistance

Item	Outline	Efficacy
Molecular weight of PE resin	Extruding workability decreases as molecular weight increases and electrochemical oxidation resistance is improved	Better
Amount of PE resin	Extruding workability decreases as amount of PE resin increases and electrochemical oxidation resistance is improved. On the other hand, porosity decreases and electrical resistance increases.	Not good
Amount of oil	Electrical resistance increases as amount of oil increases and electrochemical oxidation resistance is improved. On the other hand, separator easily becomes dirty with oil.	Not good
Backweb thickness	Electrical resistance increases as backweb thickness increases and electrochemical oxidation resistance is improved.	Not good

Table 5
General properties of PE resin

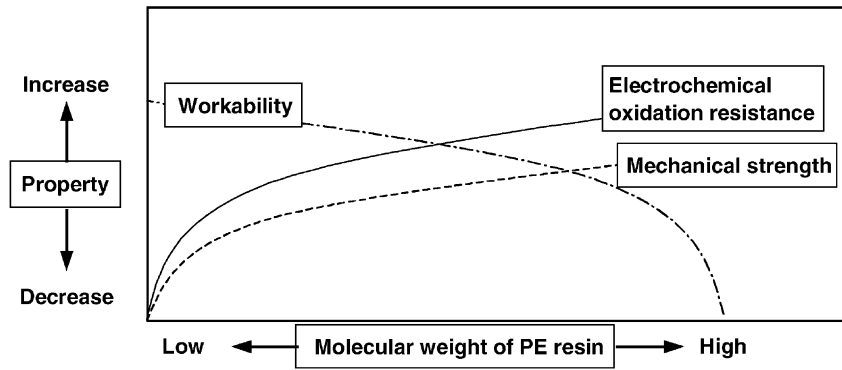| Item	Polymer PE	Super-polymer PE	Testing method
Mean molecular weight	20–100	100–600	Viscosity or GPC
Density (g/cm^3)	>0.955	>0.935	ASTM D 1505
MI (g/10 min)	>0.05	–	ASTM D 1238
Tensile yield point strength (kg/cm^2)	<300	>400	ASTM D 638
Methyl radical (ea./1000)	>3.2	<0.3	C: carbon
Vinyl radical (ea./1000)	>0.06	<0.03	C: carbon

Fig. 8. Molecular weight, electrochemical oxidation resistance, and workability of PE resin.

Table 6
Relation between molecular weight of PE and separator properties[a]

Item	Molecular weight of PE (relative value: standard material = 100)					
	50	100	115	130	150	160
Property of PE resin						
Viscosity	79	100	119	132	144	158
Melt pressure	64	100	115	187	182	210
Separator property						
Backweb thickness	0.25	←	←	←	←	←
Tensile strength	91	100	112	128	149	163
Elongation	45	100	119	113	130	123
Electrochemical oxidation resistance						
Electrochemical oxidation time	67	100	91	139	102	140
Resistance to hot sulphuric acid						
Elongation rate of initial data	97	100	153	151	140	148
Extruding workability		Better	Better	Better	Better	Not good

[a] The measurement results are shown as values relative to that of the standard material which is assumed to be 100.

and loaded at 1.96 N/cm^2. This assembly was immersed in dilute sulphuric acid (relative density 1.3) at 50 °C and a current of 5 A was applied. The time until the voltage decreased by 0.2 V or more was measured. Samples (10 mm in width and 100 mm in length) were also immersed in dilute sulphuric acid (relative density 1.6) for a given number of days. The elongation of the sample after immersion was measured and compared with initial data.

Both the tensile strength and electrochemical oxidation time (which is related to the lifetime of the battery) of the PE separator increase as the molecular weight is increased. The latter finding is shown in Fig. 9. In some cases, however, the improvement cannot be observed when the molecular weight is 1.5 times. It is assumed that this is because not only the molecular weight of PE, but also the number of the radicals and side-chains affect the performance.
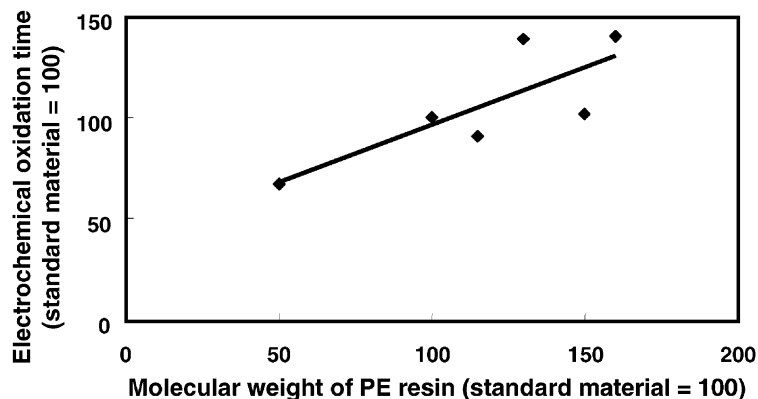

Fig. 9. Relation between molecular weight of PE resin and electrochemical oxidation time.
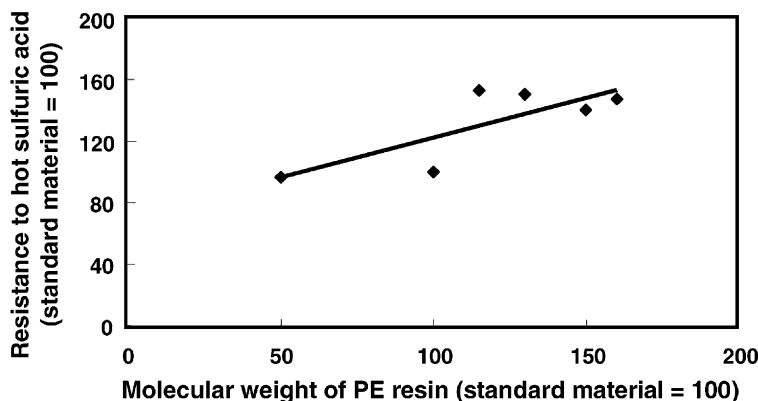
Fig. 10. Relation between molecular weight of PE resin and resistance to hot sulphuric acid.

An improvement in the elongation rate of initial data for the resistance to hot sulphuric acid is obtained by using a PE with a molecular weight of over 1.15 times that of the standard material, as shown in Fig. 10. No significant difference is observed in the range 1.15–1.6 times. Moreover, the workability is decreased markedly due to the increase in melt pressure when the molecular weight is 1.3 times or more.

5.2. PE resin content

PE resin is oxidised in an oxygen atmosphere, and the auto-oxidation starts rapidly when the concentration of hydroperoxide accumulated in the substrate of the PE exceeds a certain value. Consequently, the extension of separator lifetime by the following method can be considered. The amount of hydroperoxide formed is suppressed, and the decomposition is retarded, by decreasing the oxygen partial pressure on the PE molecules and retarding the oxygen absorption rate by increasing the PE resin content. An increase in the content causes, however, an increase in the resin pressure and leads to a decrease in the workability.

5.3. Oil content

The oil used in the PE separator is an olefinic hydrocarbon (i.e. similar to the PE resin) and is a fluid with a certain viscosity. Because this oil forms a protective film on the surface of the PE particles in the separator and, thus, serves to prevent nascent oxygen from directly touching the particles, increase in the oil content is an effective means for improving the electrochemical oxidation resistance. Also, because the oil has a molecular weight lower than that of the PE resin and is easily oxidised, the effect ends when the oil is consumed by oxidation. Moreover, the pores are closed when the oil content is increased and, therefore, the electric resistance increases. Finally, the oil can form a scum by adsorbing carbon (which is an additive in the negative electrode) as well as any active material and lead powder that are floating in the electrolyte. This can result in harmful effects such as making the surface of the electrolyte, the

battery case, etc. dirty, causing confirmation of the liquid level to become difficult, and/or clogging the filter when a stopper with a filter is used. Consequently, it is necessary to adjust the oil content to meet the specifications for the battery, in particular the content cannot be increased too much.

6. PE separator with improved electrochemical oxidation resistance

6.1. Properties of separator

Examples of the properties of PE separators which show improved electrochemical oxidation resistance by using a PE resin of higher molecular weight are given in Table 7. It is

Table 7
Properties of PE separators with improved electrochemical oxidation resistance

Item	Improved separator	Standard separator
Dimensions		
Total thickness (mm)	1.00	1.00
Backweb thickness (mm)	0.25	0.25
General properties		
Electrical resistance ($\Omega \times 100$ cm^2 per PC)	0.009	0.0009
Tensile strength (N/mm^2)		
Md[a]	15	15
CD[b]	6	7
Elongation (%)		
MD	52	50
CD	660	710
Oil content (%)	12.4	13
Oxidation properties		
Electrochemical oxidation time (h)	260	240
Resistance to hot sulphuric acid	~1.5	1.0
Tensile strength rate of initial data (%)	98	95
Elongation rate of initial data	72	47

[a] MD: machine direction.
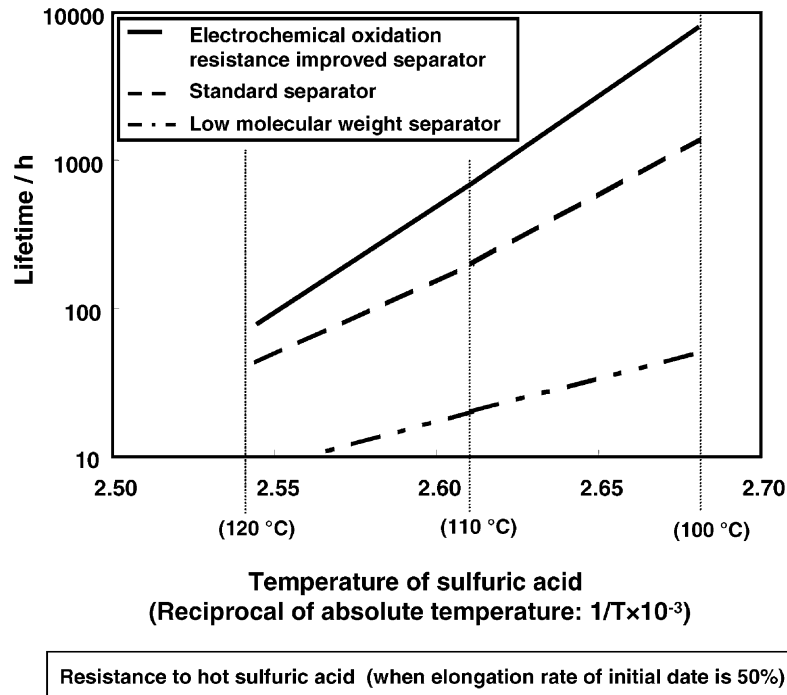[b] CD: cross direction.

Fig. 11. Relation between temperature of sulphuric acid and separator lifetime (based on Arrhenius's rule).

seen that the general properties of the improved separator are equivalent to those of a standard separator. By contrast, the electrochemical oxidation time, which corresponds to separator lifetime, is improved by about 10%, and the resistance to hot sulphuric acid, which corresponds to the degree of cracking, is increased by about 1.5 times. Note, it is understood that the oxidation resistance to hot sulphuric acid is affected by the material irrespective of the backweb thickness; consequently, even when the backweb thickness is decreased, the oxidation resistance to hot sulphuric acid is assured.

In general, because the deterioration of the material is a type of chemical reaction, Arrhenius's rule can be applied to the relation between the temperature and the deterioration rate. That is, when the reciprocal of the absolute temperature is plotted on the *x*-axis and the logarithm of the lifetime on the *y*-axis, a linear relation is obtained as a simple deterioration model.

The degree of deterioration based on the resistance to hot sulphuric acid is displayed in Fig. 11 in the form of Arrhenius plots. On exposure to sulphuric acid at 110 °C, the time required to decrease the elongation rate of initial data by up to 50% is about 3.5 times longer for the improved separator than for the standard separator.

6.2. Battery tests

Tests were performed on 55D23R-type batteries using standard separators or electrochemical oxidation resistance improved PE separators. The initial characteristics of the batteries (see Table 8) are excellent for both types of separator. There are no significant differences in the characteristics of the two separators.

SAE 75 °C life-cycle tests were performed on the batteries. The results are shown in Fig. 12. The lifetime of batteries using improved electrochemical oxidation

Table 8
Evaluation of initial characteristics of 55D23R batteries[a]

Item	Standard separator	Electrochemical oxidation resistance improved separator	
Backweb thickness (mm)	0.25	0.25	0.20
Nominal capacity at 5 h rate	100	100	100
Initial capacity at 5 h rate	100	100	100
Low temperature high-rate discharge			
Voltage (5 s)	100	101	101
Duration	100	100	101

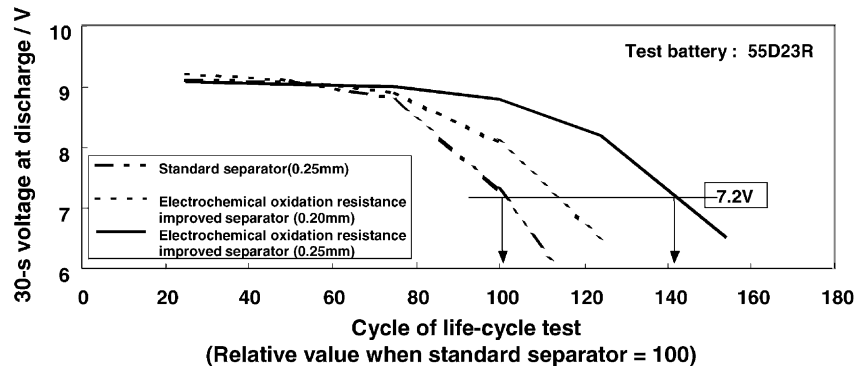[a] Relative values when standard material is assumed to be 100.

Fig. 12. Results of SAE 75 °C life-cycle test.

resistance separators is 1.44 times that of batteries using standard separators. Moreover, even a thin backweb (0.20 mm) separator has a lifetime which is 1.14 times that of the standard separator (backweb: 0.25 mm).

7. Summary of results

1. Either the SPG separator or the PE separator, each which has a low electrical resistance and a small average pore size, is suitable for lead–acid batteries with respect to engine-starting capability and the prevention of short-circuits by dislodged particles of positive active-material.
2. The SPG separator has high temperature durability and high vibration resistance and is suitable for batteries used in hot regions (i.e. tropical and subtropical regions) and under bad road conditions. In Japan, it is mainly used for the heavy-load batteries such as those for buses, trucks, and recreational vehicles. The market share of these batteries is 30%.
3. The PE separator is characterised by excellent starting capability and is suitable for a battery used under good road conditions in a clement or cold weather region. In Japan, due to the decrease in vibration of the battery caused by the improvement in road conditions and the popularisation of the MF battery, the envelope-type separator is required for expanded-type calcium electrodes. The application of this separator has spread to about 70% in batteries for common passenger cars. The separator has replaced the leaf-type SPG separator.
4. Recently, the ambient temperature of the battery has risen along with making the car more sophisticated and comfortable, and the PE separator, which can endure high temperature, has now been required.
5. We have developed an improved electrochemical oxidation resistance PE separator for batteries operated at high temperatures. The resistance to hot sulphuric acid, which is one of the oxidation-resistant characteristics, has been increased by a factor of 1.5 by using a PE resin of high molecular weight, and the deterioration due to attack by sulphuric acid at high temperature has been improved compared with the standard separator.
6. Batteries made with improved electrochemical oxidation resistance PE separators have about 1.4 times the lifetime of those with standard separators under the conditions of the SAE 75 °C life-cycle test.