

Development of Low VOC Sealant for Door Hole Seal

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ABSTRACT

A sealer has been developed to reduce the amount of volatile organic compounds (VOC) in automotive cabins. This sealer can be discharged at 60 °C and enhances film retention. During development workability and work safety were taken into account.

Partially cross-linking styrene butadiene rubber (SBR1) has been used to replace butyl rubber as the main component of the sealer. This replacement ensures dischargeability of the sealer, eliminating the need for the solvent additive formerly used to do so. These changes have increased the Thixo index of the material when heated, enabling both dischargeability at 60 °C and film retention to be achieved.

Non-crosslinking styrene butadiene rubber (SBR2) has also been used as a component of the sealer to increase heat resistance.

This new sealer contributes to meeting the standards for the “Voluntary Approach to Vehicle Cabin VOC Reduction.” These standards are slated to be applied to new model passenger cars marketed from April 2007.

1. Introduction

Currently, the most common materials used to seal car door holes are tape, a high-temperature discharge sealer (90 °C to 150 °C)⁽¹⁾, ⁽²⁾, and a normal-temperature discharge sealer with enhanced workability. Recently, however, there have been demands for decreased use of volatile organic compounds (VOC) in vehicle cabins.

For the 2006 model of the Civic (Fig. 1), Honda is using a door panel that opens wide and has excellent manufacturability and maintenance characteristics.

However, because the panel opening is wide, it was necessary to find a way to reduce cabin noise, such as road noise, caused by this large opening. To address the noise issue, a new hole seal was developed that includes a sound insulating sheet. As a result, a new sealer with enhanced retention was required that would correspond to the weight increase of the film.

This report describes the development of a low-VOC sealer, able to be discharged at 60 °C, that maintains the current degree of

workability while providing enhanced film retention at high temperatures.



Fig. 1 Door panel

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2. Development Goals

Sealer used to seal door holes⁽³⁾ prevents rain from entering the vehicle cabin by forming a seal between the door's inner panel and the hole seal. The inside of the door can reach temperatures of almost 70 °C in summer; therefore, in addition to maintaining sealing ability at high temperatures, it must also maintain film retention.

Furthermore, during maintenance of components inside the door panel, the hole seal must be able to be removed; therefore, a material that can be reinstalled after completing this maintenance needed to be used.

In conjunction with development of this new sealer, the following 5 items were defined as development goals.

- (1) No solvents added to the material
- (2) Good retention performance of the hole seal film at high temperatures
- (3) A discharge temperature of 60 °C or less for worker safety
- (4) Can be reinstalled for maintenance
- (5) Favorable workability at the assembly plant

3. Concept for the Basic Specifications of the Sealer Material

Figure 2 shows a design concept for a sealer material that would enable film retention at high temperatures, good discharge performance, and reinstallation. The figure also includes the goal range for each of these characteristics. Characteristics for normal-temperature discharge sealers (Current 1) and high-temperature discharge sealers (Current 2), that are currently in widespread use, are shown for reference.

This figure shows that the materials that are currently used fall within some of the goal ranges, but do not meet all of the goal specifications. This meant that the development concepts could be narrowed down to achieving good dischargeability and retention.

To ensure good retention at high temperatures, the static viscosity of the material (viscosity when shear speed is low) must be high. Additionally, to ensure good discharge performance, the dynamic viscosity (viscosity when shear speed is high) must be low⁽⁴⁾. In other words, it was believed that a high thixotropy index would be

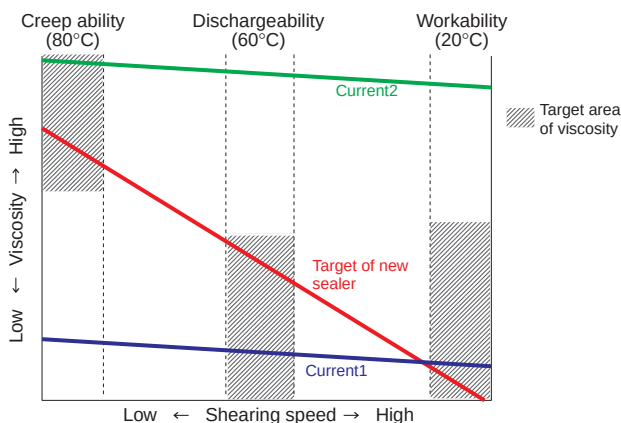


Fig. 2 Concept of viscosity design

needed, in addition to a viscosity that would enable sufficient discharge.

To develop a sealer material easily affected by shear speed, the investigation began by looking at rubber, which is the main component of sealers. In choosing a rubber compound, emphasis was placed on versatility, leading to the selection of butyl rubber (IIR), styrene-butadiene rubber (SBR), and acrylonitrile-butadiene rubber (NBR) for investigation. IIR, which is currently in use, has a relatively linear molecular structure, and the change in viscosity relative to shear speed is low. SBR and NBR, on the other hand, have functional groups at its' terminals and therefore have relatively high polarity⁽⁵⁾. The functional groups at the terminals of these rubber compounds generate an interaction between molecules. Therefore, at low shear speeds high viscosity is achieved and interaction is maintained; while at high shear speeds, interaction is interrupted and viscosity decreases.

Note that to ensure low levels of VOC, essentially none were to be added. Therefore development proceeded without the use of a solvent.

4. Evaluation Method

To evaluate the actual performance of the sealer, viscosity was used to judge dischargeability, a repeated peel test of the film was used to test reinstallation capability, and a high-temperature creep test method, shown in Fig. 3, was used to confirm the high-temperature retention performance.

For the high-temperature creep evaluation, a 180° peel creep resistance test and a shear creep resistance test were conducted. During the shear creep resistance test the load is dispersed over the whole surface. On the other hand, during the 180° creep resistance test there is a higher tendency for stress to be concentrated at the adhered surface, thus providing more severe test conditions. This report only presents the results of the 180° peel creep resistance test.

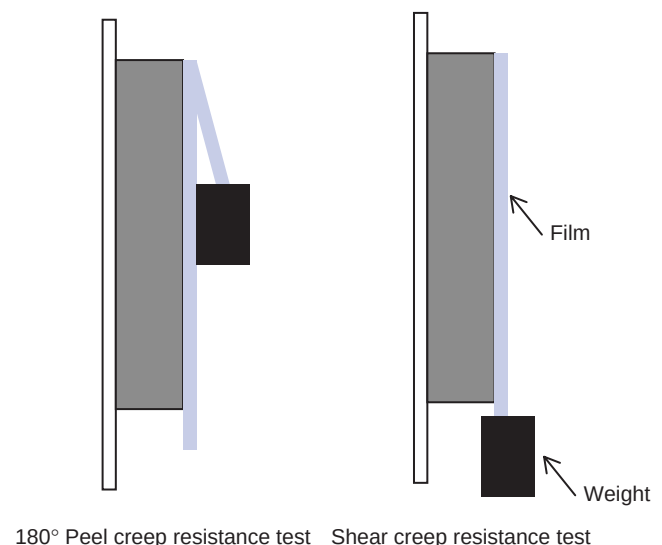


Fig. 3 Creep resistance test method

Table 1 Selection of main rubber

Rubber	180° Peel creep resistance 0.5g, 80°C24h	Viscosity (60°C)	Reinstallation (after heat resistance)
NBR1	5.0mm	60Pa·s	Water leakage Adhesive failure
NBR2	10mm	65Pa·s	Water leakage Cohesive failure
SBR1	1.0mm	59Pa·s	Water leakage Adhesive failure
SBR2	4.0mm	62Pa·s	Water leakage Cohesive failure
IIR	20mm	67Pa·s	Water leakage Cohesive failure

Table 2 Selection of secondary rubber

Rubber	Effect	Result			
		Reinstallation (after heat resistance)	Storage stability (Coefficient of rate of change of viscosity)	Creep ability	Workability
Blank	—	Water leakage Adhesive failure	+30%	1.0mm	Adequate
IIR	Heat resistant	Water leakage Cohesive failure	+5%	2.5mm	Inadequate
NBR2	Heat resistant	Water leakage Cohesive failure	+4%	4.0mm	Adequate
SBR2	Heat resistant	No Water leakage	+5%	1.0mm	Adequate

5. Consideration and Results for the Basic Specifications of the Sealer Material

5.1. Investigation of Achievement of Both Dischargeability and Film Retention at High Temperatures

Table 1 shows results from an investigation that used the three development goals, described previously, to select a main rubber compound.

For NBR and SBR, an investigation was performed of partially heated and cross-linking type (NBR1, SBR1) and non cross-linking type (NBR2, SBR2). For IIR, only non cross-linking types were investigated.

The results showed that SBR1 performed the best. The reason for this is thought to be as follows; to achieve the development goals shown above, a sealer with a higher thixo index than conventional sealers is needed. The SBR1 has localized and dispersed cross-linkings, therefore it is more affected by shear speed, thus having a higher thixo index.

A heat resistance test showed that when only SBR1 was used, cross-linking progressed during the heating process, and reinstallation was no longer feasible; therefore, it was decided to enhance the heat stability of the material.

5.2. Enhancement of Heat Stability

The effect of combining another rubber with the SBR1 main rubber was investigated as a means of enhancing the heat stability of the material.

Table 2 shows the results. Parameters for heat stability, reinstallation characteristics, storage stability and workability were measured. In addition, the initial purpose of film retention at high temperatures was also confirmed.

When combined with non-cross-linking IIR, NBR2, or SBR2, good storage stability results were obtained. This is possibly because combining SBR1 with non-cross-linking rubber compounds reduced the percentage of rubber that was cross-linked overall. Any reduction in the percentage of rubber that was cross-linked using this rubber combination, compared to when the partially cross-linking SBR1 was used alone, could be due to a suppression of the progress of the cross-link reaction caused by heat.

Next, concerning high-temperature creep resistance and water tightness, combinations using either IIR or NBR2 did not have sufficient cohesive strength and therefore did not satisfy water tightness requirements. In addition, compared to SBR2, the amount of creep increased. As a result, it was decided to use a combination of SBR1 and SBR2.

5.3. Investigation of Compositions

The proportional ratios for high-temperature creep resistance and storage stability between SBR1 and SBR2 were investigated. Figure 4 shows the relationship of high-temperature creep resistance and storage stability with respect to the proportion of SBR1, as well as goal ranges for high-temperature creep resistance and storage stability (within the shaded area).

The amount of creep is more favorable with increased amounts of SBR1, but storage stability decreases. This is thought to be because cross-linking, attributed to heat resistance, increased the viscosity when SBR1 was used alone. As the amount of SBR2 increased, creep resistant performance was reduced due to insufficient cohesive strength. Note that the final combination amount was set within the range shown by the shaded area.

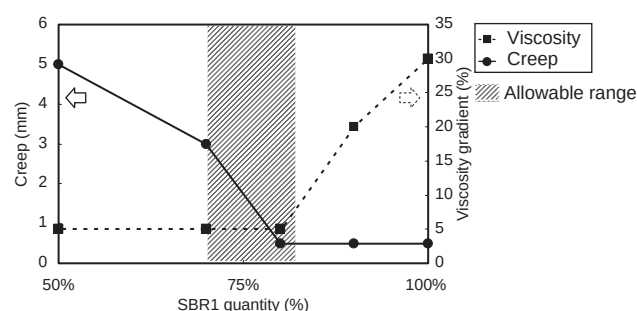


Fig. 4 Effect of SBR1 composition

6. Material Test Results

6.1. Dischargeability

Figure 5 shows viscosity characteristics of the newly developed and conventional sealer materials. The working temperature of the developed material is 60 °C and that of the conventional material is 20 °C.

The viscosity at high shear rates of the developed material is lower than that of the conventional material, and therefore it was expected that dischargeability would be favorable. On the other hand, in the low shear rate region, viscosity is high and therefore creep performance is thought to be enhanced.

As a result of confirming dischargeability using a hand gun and mass production equipment, the discharge performance was found to be favorable.

6.2. High-temperature Creep Resistance Test

As an indicator of film retention, a 180° peel high-temperature creep resistance test was performed, and Fig. 6 shows the results.

The creep resistant performance of the rubber composition

selected from the previously described investigations was found to be better than that of the conventional material. In addition, by combining an inorganic agent, the final material has an increased thixo index at high temperatures, further enhancing creep resistant performance. As a result, during heat load, with respect to the goal of 3 mm or less for the amount of creep, an amount of creep of nearly 0 mm was achieved.

6.3. Door Hole Sealer VOC Measurement Results

Figure 7 shows VOC measurement results for the newly developed and conventional materials. The measurement method was established for each part based on Japan Automobile Manufacturer's Association, Inc. methods^{(6), (7)}, and the data was

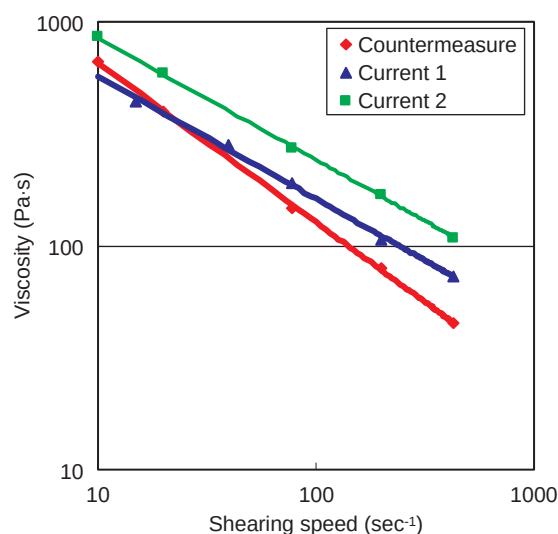


Fig. 5 Shear rate curve

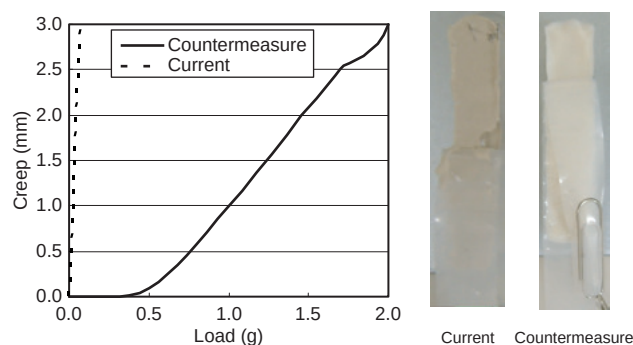


Fig. 6 Creep resistance test result

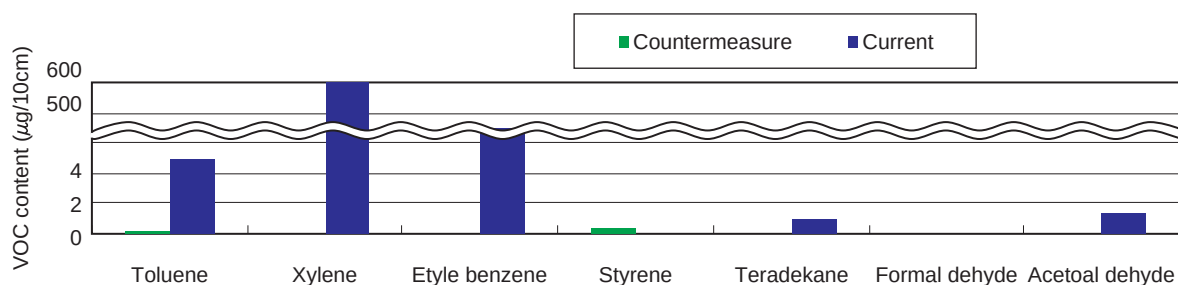


Fig. 7 VOC test result (unit)

evaluated using a Honda-specific method. After the solvent used to adjust viscosity and ensure workability was removed, the amount of xylene and ethyl benzene in the developed material was reduced to less than 1/7000 of that of the conventional material.

7. Results of Tests on an Actual Vehicle

7.1. Compatibility with Actual Vehicle

A heat cycle test was performed on the door of an actual vehicle. The test mode is shown in Fig. 8 and the test results after 5 cycles are shown in Fig. 9. In the previously described high-temperature creep resistance test, the film and sealer were in an unconstrained open system. In this test, the sealer was applied around the entire circumference of the door hole and pasted together with the film, making it a constrained system. Therefore, as the film itself stretches and contracts due to heat cycling, this is a composite test that considers displacement of the film in addition to retention at high temperature. The newly developed sealer material, exhibiting the same behavior as in the component level high-temperature creep resistance test, did not have any creep and it was not affected by the stretching and contracting of the film, leaving no issues to be addressed.

In addition, compared to initial application, there was no significant change in stringing when the film was peeled off after the durability test, and there was no water leakage after reinstallation. This led to the conclusion that there were no issues with regards to maintenance capability.

7.2. Actual Vehicle VOC results

A vehicle was left in an airtight condition for 14 days after manufacturing and the VOC was then measured. The measurement method followed the Japan Automobile Manufacturers

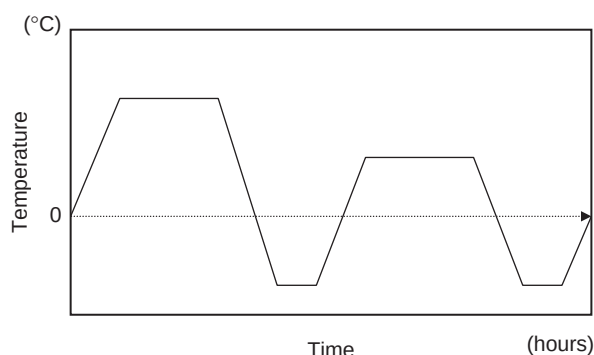


Fig. 8 Heat cycle mode



Fig. 9 Heat cycle test result (door panel)

Association's measurement method. Through the application of the newly developed sealer, concentrations of xylene and ethyl benzene met standard values.

8. Conclusion

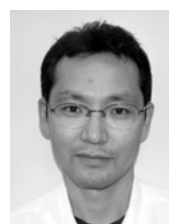
A sealer with low levels of VOC that ensures enhanced retention of the film as well as maintaining the same workability as conventional sealer materials has been developed and the following results were obtained.

- (1) A partially cross-linking SBR rubber compound was selected. Discharge at high temperatures, equivalent to that of conventional materials, was achieved through increasing dependence on shear speed. In addition, the thixo index at high temperatures was enhanced, enabling better retention of the film.
- (2) Investigation of the composition of partially cross-linking and non cross-linking materials enabled the control of cross-link reaction due to heat resistance, while creep resistant characteristics were maintained. This led to enhanced storage stability.
- (3) Due to the fact that solvents were not used in the manufacturing of this new sealant, concentrations of xylene and ethyl benzene inside the vehicle cabin met Japan Automobile Manufacturer Association standards.

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