

Development of Low Volatile Organic Compound Dust Sealing Material

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ABSTRACT

A dust sealing material displaying low levels of volatilization of acetaldehyde and toluene has been developed in order to enhance the air quality of automobile cabins. Volatilization of acetaldehyde has been reduced by more than 90% and that of toluene by more than 45% in the developed dust sealing material, as compared to the former sealing material.

As component materials, an acrylic resin and a urethane resin have been used for the base resin of the sealing material, and a toluene-free diluent has been employed. From the perspective of the production method, the use of toluene has been discontinued in the production processes of all materials to help eliminate any residual toluene content. In addition, the use of solvents containing toluene has been discontinued in the factories where the dust sealing material is produced, and the level of toluene in the air in the factories has been controlled to a specified level or below.

1. Introduction

In order to enhance air quality by reducing volatile organic compounds (VOC) such as formaldehyde, acetaldehyde, and toluene from automobile cabins, in February 2005 a voluntary approach to vehicle cabin VOC reduction was announced by the Japan Automobile Manufacturers Association(JAMA)⁽¹⁾. Under this voluntary approach, Japanese auto manufacturers will attempt to satisfy guideline figures for the 13 substances shown in Table 1 stipulated by the Ministry of Health, Labour and Welfare in new vehicle models marketed from 2007, and will attempt to achieve further reductions in later models.

Reducing VOC emissions from cabin components is one method of reducing the VOC level of automotive cabins. Therefore, an effective method of reducing VOC levels is to focus on materials that display a high level of VOC emissions and are extensively used, and on components that are commonly used. An example is a sealant for door hole seals displaying reduced xylene and ethyl benzene volatilization⁽²⁾ which has been developed and has gone into use.

Approximately 80 components used in automotive cabins were studied with regard to VOC emissions and multiple uses. As shown in Table 2, the results of this study indicated that volatilization of acetaldehyde and toluene from dust sealing materials displayed a high rate of contribution to cabin VOC levels, regardless of vehicle type.

Dust sealing materials are applied in the coating

Table 1 Materials selected for indoor density level reductions to comply with Ministry of Health, Labor and Welfare guidelines

No	Materials
1	Formaldehyde
2	Acetaldehyde
3	Toluene
4	Xylene
5	Ethylbenzene
6	Styrene
7	Tetradecane
8	Di-n-butyl phthalate
9	Di-2-ethylhexyl phthalate
10	Paradichlorobenzene
11	Chlorpyrifos
12	Diazinon
13	Fenobucarb

Table 2 Contribution rate of dust sealer to indoor VOC

Vehicle type	Acetaldehyde (%)	Toluene (%)
Sedan A	15	13
Sedan B	13	6
SUV A	23	6
SUV B	15	9

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Table 3 Acetaldehyde volatilization and contribution rate of raw materials

Basic raw material	Concentration of acetaldehyde volatilization		Contribution rate of acetaldehyde volatilization %
	$\mu\text{g}/1\text{ g raw material}$	$\mu\text{g}/1\text{ g dust sealer}$	
PVC homopolymer	1	0.10	8.6
PVC/PVAc copolymer	10	1.00	85.9
Plasticizer	0.05	0.02	1.3
Filler	0.05	0.02	1.9
Diluent	1	0.02	1.7
Adhesive agent	0.3	0.01	0.5
Moisture absorption prevention agent	0.01	0.00	0.0
Total		1.16	100

Table 4 Alternative resin from PVC/PVAc copolymer

Resin		PVC homopolymer	Acrylic resin	Urethane resin	Epoxy resin
Material properties	Tensile strength	Good	Poor	Good	Excellent
	Elongation	Good	Good	Excellent	Fail
Workability	Applicability	Good	Good	Fail *2	Fail
	Storage stability	Good	Good *3	Good	Poor
Environment		Fail *1	Good	Good	Good
Cost		Low	Middle	High	High

*1 Increased chlorine density in automobile shredder residue.

*2 Difficult to lower viscosity due to plasticizer mixing.

*3 Use of acrylic resin core shell structure.

process of automobile manufacture to prevent water infiltrating the vehicle cabin from the joints between the steel sheets. The same dust sealing material is normally used in all the vehicles produced on a single assembly line. The development of a dust sealing material displaying low volatilization of acetaldehyde and toluene would therefore be an effective means of reducing cabin VOC levels.

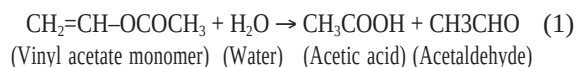
This paper reports on the development of a dust sealing material that displays lower levels of acetaldehyde and toluene volatilization than that of the conventional sealing material.

2. Reduction of Acetaldehyde

As shown in Table 3, the concentration of volatilized acetaldehyde in 1 g of each of the constituents of the conventional dust sealing material were measured in order to specify the cause of volatilization of this substance from the material. The rate of contribution of each constituent of the dust sealing material to the concentration of volatilized acetaldehyde was calculated based on the results of these measurements and the composition of each constituent. The results of this study indicated that a copolymer of vinyl chloride and vinyl acetate (PVC/PVAc copolymer) displayed the highest rate

of contribution, and this copolymer was therefore specified as the main cause of acetaldehyde volatilization.

A vinyl acetate monomer is used as a raw material in the production of the PVC/PVAc copolymer, and it is conjectured that some of this monomer is hydrolyzed in the reaction shown in Eq. (1) and taken up in the copolymer as an impurity.



Following this, methods of substituting another resin for the PVC/PVAc copolymer were studied to reduce the acetaldehyde content of the dust sealing material. The dust sealing material is applied following e-coating of the white body, and is cured in two ovens, for the primer surfacer and top coat, and the substitute resin was therefore required to be a resin that is cured by heating.

Table 4 shows the characteristics of standard resins of this type. The substitution of a vinyl chloride homopolymer for the PVC/PVAc copolymer would represent a low-cost solution, and material properties and workability would also match requirements. However, the Law for the Recycling of End-of-Life Vehicles, which took effect in January 2005, stipulates that the recycling rate of shredder dust must be increased to 70% or higher by 2015⁽³⁾. It is therefore not desirable from the viewpoint

Table 5 Toluene volatilization and contribution rate of raw materials

Basic raw material	Concentration of toluene volatilization		Contribution rate of toluene volatilization %
	$\mu\text{g}/1\text{ g raw material}$	$\mu\text{g}/1\text{ g dust sealer}$	
PVC homopolymer	0.5	0.05	0.1
PVC/PVAc copolymer	1.5	0.15	0.4
Plasticizer	0.5	0.15	0.4
Filler	0.0	0.00	0.0
Diluent	2000	40.00	98.6
Adhesive agent	10	0.20	0.5
Moisture absorption prevention agent	0.0	0.00	0.0
Total		40.55	100

of recycling to increase the amount of the vinyl chloride homopolymer to a level higher than that of the conventional dust sealing material.

The possibility of substituting urethane resins or epoxy resins was also low from considerations of workability and cost.

Acrylic resins possess slightly less tensile strength than vinyl chloride homopolymers, but would be candidates as substitute materials if their tensile strength could be increased. Urethane resin, which possesses excellent tensile strength and elongation, and a curing agent were therefore added to acrylic resin, and the effect on the tensile strength of the dust sealing material was studied. The results are shown in Fig. 1. As Fig. 1 shows, the use of a higher ratio of urethane resin to acrylic resin, in addition to the addition of urethane resin and a curing agent that equalized their reaction ratios, has resulted in an increase in the tensile strength of the dust sealing material.

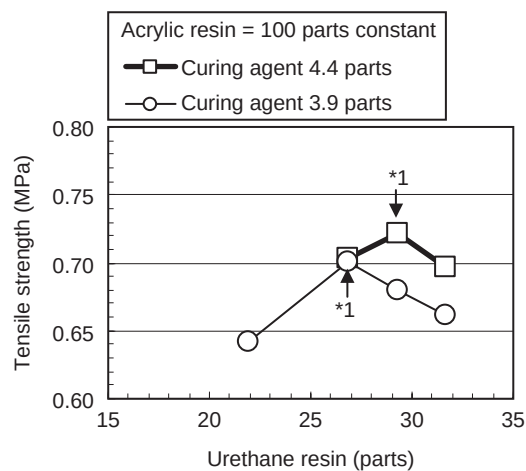
In addition to replacing the PVC/PVAc copolymer with an acrylic resin and a urethane resin, this

development project also eliminated the vinyl chloride homopolymer employed in the conventional dust sealing material in order to enable simpler recycling of the shredder dust.

3. Reduction of Toluene

As in the case of analysis of acetaldehyde volatilization, the concentration of volatilized toluene in 1 g of each of the constituents of the dust sealing material was measured, and the rate of contribution of each constituent of the dust sealing material to the concentration of volatilized toluene was calculated from the measurement results and the composition of each constituent. The results are shown in Table 5. The diluent displayed the highest rate of contribution, and this constituent was therefore specified as the main cause of toluene volatilization. A number of organic solvents are mixed in the diluent, one of which is toluene. This project therefore used a diluent that did not contain toluene.

The effect of the adhesion promoter, which displayed



*1 Equivalent reaction ratio of urethane and curing agent

Fig. 1 Compound ratio and tensile strength of acrylic resin, urethane, and curing agent

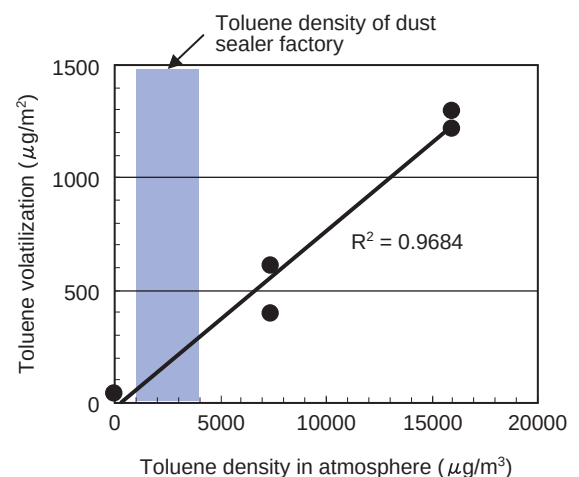


Fig. 2 Influence of toluene density in atmosphere on toluene volatilization

Table 6 Acetaldehyde and toluene volatilization of raw materials

Basic raw material	Concentration of acetaldehyde volatilization		Concentration of toluene volatilization	
	$\mu\text{g}/1\text{g}$ raw material	$\mu\text{g}/1\text{g}$ dust sealer	$\mu\text{g}/1\text{g}$ raw material	$\mu\text{g}/1\text{g}$ dust sealer
Acrylic resin	0.1	0.02	2.5	0.38
Urethane resin and curing agent	0.1	0.01	3.5	0.21
Plasticizer	0.2	0.07	1.5	0.45
Filler	0.0	0.00	0.0	0.01
Diluent	0.0	0.00	0.1	0.00
Moisture absorption prevention agent	0.0	0.00	0.0	0.00
Total		0.10	Total	1.05

a low rate of contribution to the concentration of volatilized toluene but contained a large amount of toluene, was next examined. Toluene is used as a solvent in the production of the adhesion promoter, it was therefore assumed that toluene was incorporated in the substance as impurities. Toluene was therefore also eliminated from the production process of the various constituents used in the developed material.

However, in many cases, solvents containing toluene are used to clean production equipment, pipes, etc. in the factories where dust sealing materials are produced. The toluene concentration in the air in the factories is 1000-4000 $\mu\text{g}/\text{m}^3$. The possibility of the toluene present in the air being incorporated in the dust sealing material during the production process was therefore investigated. As Fig. 2 shows, a correlation was determined between the concentration of toluene in the air and toluene volatilization from the dust sealing material. In parallel with this development project, solvents containing toluene were therefore eliminated from the factories where dust sealing materials are produced, and the concentrations of toluene in the factories have been controlled to a specified level or below.

4. Performance of Developed Material

Table 6 shows the results of measurements of the acetaldehyde and toluene volatilization concentrations in 1 g of each of the constituents of the newly developed dust sealing material. Based on these results and the composition of each constituent, 1 g of the dust sealing material was calculated to contain 0.10 μg of acetaldehyde. Using the same method, 1 g of the material was calculated to contain 1.05 μg of toluene.

Test pieces were formed using the newly developed and conventional dust sealing materials as shown in Fig. 3, and the volatilization concentrations of acetaldehyde and toluene were measured. The results are shown in Fig. 4. In comparison to the conventional dust sealing material, acetaldehyde volatilization has been reduced by more than

90% and toluene volatilization by more than 45% in the newly developed material.

The performance of the material as a dust sealing material was next examined. The material properties of the conventional and newly developed dust sealing materials were compared using the automotive sealant test method specified by JASO M323-86. The results are shown in Table 7. The newly developed sealing material displayed identical material properties to the conventional sealing material, indicating its potential for use as an automotive dust sealing material.

The use of the developed low-VOC dust sealing material enabled vehicle cabin VOC levels to satisfy the voluntary standards adopted by JAMA⁽¹⁾, and the

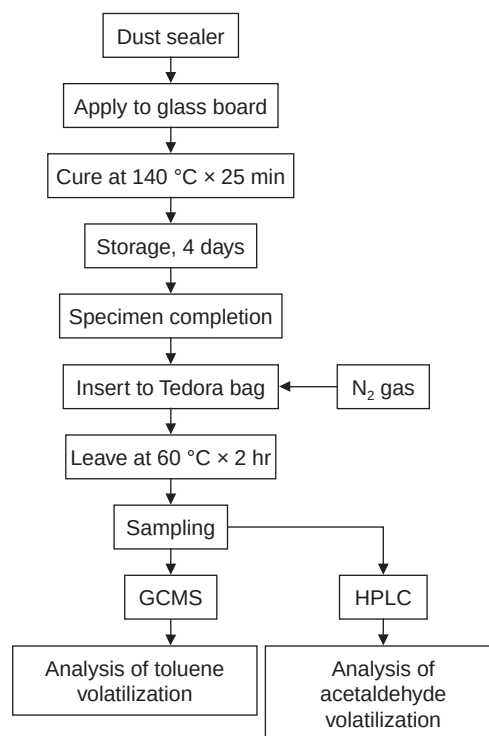


Fig. 3 Measurement method of volatilization

Table 7 Material performance

No	Confirmation item	Developed material	Conventional material
1	Tensile strength	1.3 MPa	1.3 MPa
2	Elongation	290%	150%
3	Shearing adhesion strength	1.4 MPa	1.3 MPa
4	Hardness	74	82
5	Water resistance	1.2 MPa	1.2 MPa
6	Low temperature resistance	Acceptable	Acceptable
7	High temperature adhesion strength	0.60 MPa	0.40 MPa
8	Vibration resistance	Acceptable	Acceptable
9	Watertightness	No water leakage	No water leakage
10	Viscosity	100 Pa·s	90 Pa·s
11	Storage stability	107 Pa·s	97 Pa·s
12	Fluidity	0 mm	0 mm
13	Self-leveling characteristics	No color transparency	No color transparency
14	Coating pollution	Acceptable	Acceptable

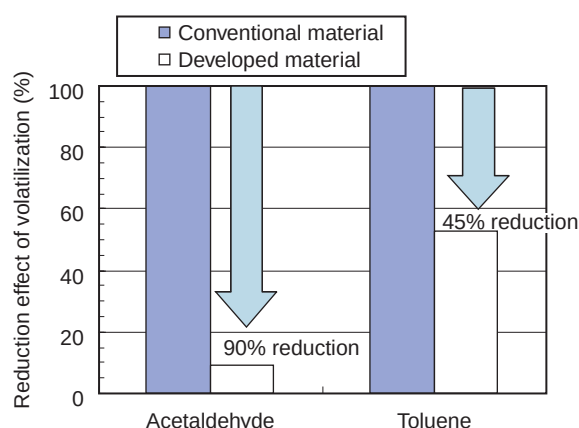


Fig. 4 Reduction effect of acetaldehyde and toluene

developed sealing material has been confirmed as having contributed to a reduction in VOC emissions in automobile cabins.

5. Conclusion

The following are the salient points in the development of a low-VOC dust sealing material that displays low concentrations of volatilized acetaldehyde and toluene.

- (1) In order to control production of acetaldehyde and to increase the ease of recycling of shredder dust, vinyl chloride was eliminated by changing the base resin to an acrylic resin from PVC/PVAc copolymer and a vinyl chloride homopolymer. In addition, urethane resin was also employed to increase tensile strength to a level matching that of the conventional sealing material.

- (2) A toluene-free diluent was used.
- (3) The use of toluene in the production process of the constituents of the dust sealing material was shown to result in the incorporation of toluene into the constituents as impurities, and toluene was therefore eliminated from the production process.
- (4) Toluene is present in the air of factories where dust sealing materials are produced and is incorporated in sealing materials. Therefore, the use of solvents containing toluene has been discontinued, and the level of toluene in the air in the factories has been controlled to a specified level or below.

References

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