アリルカラシ油の金属類,ゴム及びプラスチックに対する腐食性並びにプラスチックフィルムに対する蒸気透過性

誌名	食品衛生学雑誌
ISSN	00156426
巻/号	363
掲載ページ	p. 375-382
発行年月	1995年6月

Corrosiveness of Allyl Isothiocyanate towards Metals, Rubbers and Plastics and Ability of Allyl Isothiocyanate Vapor to Permeate Plastic Films

(Received December 13, 1994)

Yasushi SEKIYAMA, Yuichi MIZUKAMI and Asami TAKADA

(WOS Operation, New Business Development, The Green Cross Corporation: 1-1-47, Chuoh, Johtoh-ku, Osaka 536, Japan; Head Office: 1-3-3, Imabashi, Chuoh-ku, Osaka 541, Japan)

Allyl isothiocyanate (AIT), the main flavoring component of wasabi and mustard, is reported to have strong antimicrobial activity. A study was made of the corrosive effects of AIT vapor on various substances such as metals and rubbers, and of its ability to permeate food packaging films.

It was found that allyl isothiocyanate vapor had no corrosive effect at concentrations of less than 100 ppm. At the high concentration of 3,000 ppm, however, corrosion was observed in neoprene rubber, and in all plastics except polyolefin resins, polyacetal, nylon and Teflon.

AIT was found to have a moderate ability to permeate food packaging films made of polyethylene and polypropylene, with permeability inversely proportional to film thickness.

Key words: allyl isothiocyanate, antimicrobial activity, permeability, corrosive effect, food packaging film

Introduction

In a previous report[1], the authors described the stability under various conditions and the vapor pressure changes of allyl isothiocyanate (hereinafter AIT), as part of an investigation aiming to utilize the antimicrobial effect of this substance for industrial purposes. However, before antimicrobial treatments based on AIT vapor can be introduced, the physical properties of AIT need to be investigated, such as corrosiveness of the vapor towards food packaging machines and materials, and ability to permeate food packaging films. The reactivity of AIT with heavy metals such as copper and tin has been reported to some extent in the Japanese Food Additive Standards[2], but other details of its corrosive properties are not known. Investigation of these physical properties is important not only because of AIT's above-mentioned possible effects on food packaging materials and machinery, but also to assist in the development of a device for generating fixed volumes of AIT vapor. It is also essential to know the permeability to AIT vapor of such typical packaging films as polyethylene (PE), polypropylene (PP) and nylon in order to be able to control the vapor concentration within the package so as to achieve an antimicrobial effect without leaving behind any odor.

The experiments described below were designed to assist in the identification of materials which would be resistant to corrosion by AIT and of wrapping materials which would allow the required degree of permeation by AIT vapor.

Materials and Methods

1. *Materials*

AIT (special grade) was supplied by Nakarai Tesque, purity 99.9%. The materials used in the corrosion test are listed in Table 1.

2. *Reagents*

All reagents used were special grade commercial products.

Table 1. Materials Used in AIT Corrosion Test

Metals	Plastics	Rubbers
1. Stainless steel 304	10. PE	21. Natural rubber
2. Stainless steel 316	11. PP	22. Butyl rubber
3. Tin plate	12. PC	23. Neoprene rubber
4. Brass	13. PA6	24. Silicone rubber
5. Iron	14. AS	
6. Copper	15. ABS	
7. Aluminum	16. Acrylic resin	
8. Can lids	17. PS	
9. Solder	18. POM	
	19. K resin	
	20. Teflon	
	21. Vinyl chloride	
	22. Urethane	

Table 2. GLC Conditions for AIT Analysis

Detector:	FID
Column:	glass (inner diameter: 3 mm, length: 2.6 m) 20% polyethylene glycol 20 M/Chromosorb (60–80 mesh)
Column temperature:	160℃
Injection temperature:	200℃
Detector temperature:	200℃
Carrier:	N_2 (60 ml/min)

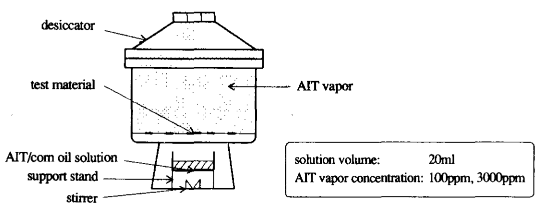

Fig. 1. AIT vapor exposure method

3. Equipment

Gas chromatograph (GC): Shimadzu Seisakusho, model GC14A.

4. Corrosion Test

The test materials were exposed in a desiccator to a fixed concentration of AIT vapor (see Figure 1) for periods of up to 20 days, and examined on removal for any softening or deformation, or absorption of AIT. Two levels of AIT vapor concentration, 100 ppm and 3,000 ppm, were tested. An untreated sample was used as the control. The examinations were performed without artificial aids.

5. Permeability Test

Determination of permeability to AIT vapor was carried out via three different methods with differing principles of measurement.

① Evaluation via the Dish Method using various packaging materials

The permeability of the materials listed below to AIT vapor was measured using a method based on the Japan Industrial Standard (JIS)[3] Dish Method for determination of the water-vapor transmission rate of moisture-proof packaging materials. Measurements were taken after 24 hours and 48 hours.

1) Monolayer films: PET (polyethylene terephthalate), CPP (cast polypropylene), OPP (oriented polypropylene), PE, nylon, EVA (ethylene vinylacetate copolymer).

2) Composite films: PP/PE blend

3) Laminated films: non-woven fabric laminated with PET; wood-free paper laminated with PET; PE-laminated paper.

4) Paper: wood-free paper; glassine paper

② Evaluation with special apparatus using PE and PP film

Using four samples of packaging film (20 μm

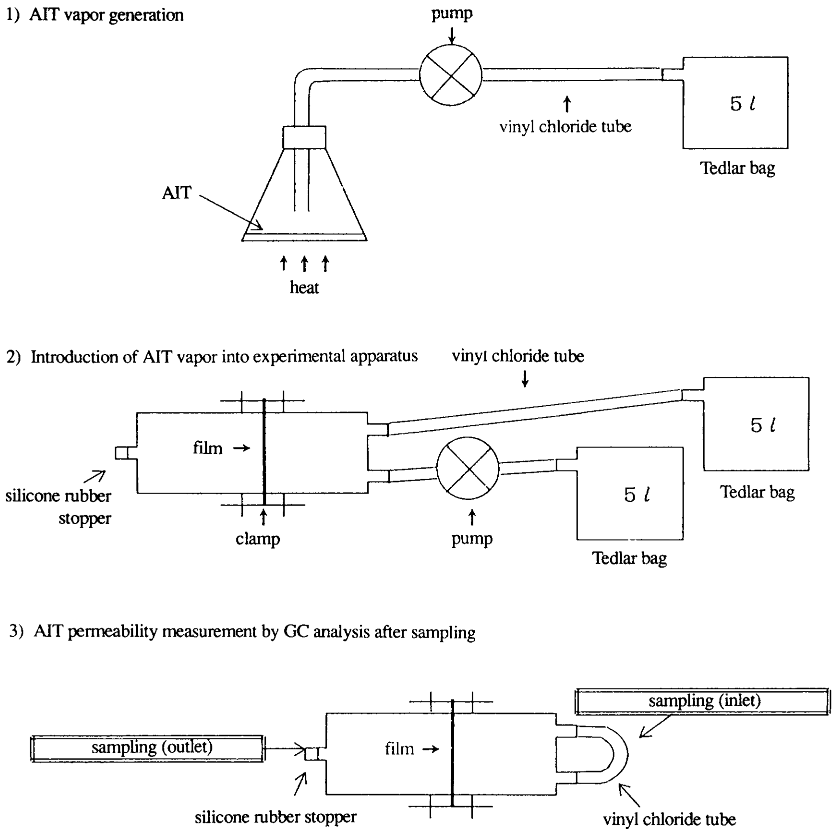

Fig. 2. Special apparatus for permeability test of PE/PP film

Table 3. Corrosive Effect of 100 ppm AIT Vapor on Various Materials

Type	Material	Test results					
		Deformation		Softening		AIT absorption	
		1 day	20 days	1 day	20 days	1 day	20 days
Metals	Stainless steel 304	—	—	—	—	—	—
	Stainless steel 316	—	—	—	—	—	—
	Tin plate	—	—	—	—	—	—
	Brass	—	—	—	—	—	—
	Iron	—	—	—	—	—	—
	Copper	—	—	—	—	—	—
	Aluminum	—	—	—	—	—	—
	Can lids	—	—	—	—	—	—
	Solder	—	—	—	—	—	—
Plastics	PE	—	—	—	—	—	—
	PP	—	—	—	—	—	—
	PC	／	／	／	／	／	／
	PA6	—	—	—	—	—	—
Rubbers	Fluorinated rubber	—	—	—	—	—	—

—: No effect; ／: Not tested

Table 4. Corrosive Effect of 3,000 ppm AIT Vapor on Various Materials

Type	Material	Test results: Deformation 1 day	Deformation 20 days	Softening 1 day	Softening 20 days	AIT absorption 1 day	AIT absorption 20 days	Comments
Metals	Stainless steel 304	–	–	–	–	–	–	
	Stainless steel 316	–	–	–	–	–	–	
	Tin plate	–	–	–	–	–	–	
	Brass	–	–	–	–	–	–	
	Iron	–	–	–	–	–	–	
	Copper	–	–	–	–	–	–	
	Aluminum	–	–	–	–	–	–	
	Can lids	–	–	–	–	–	–	
	Solder	–	–	–	–	–	±	Slight surface whitening
Plastics	PE	–	–	–	–	+	+	
	PP	–	–	–	–	–	–	
	PC	+	+	+	+	+	+	Slight liquefaction of white surface impurity
	PA6	–	–	–	–	–	–	
	AS*	⧺	/	⧺	/	+	/	
	ABS*	⧺	/	⧺	/	+	/	
	Acrylic resin	±	+	–	+	±	+	Gradual liquefaction and yellowing of surface
	PS*	⧺	/	⧺	/	+	/	Surface liquefaction and opacity
	POM	–	–	–	–	–	–	
	K resin*	⧺	/	⧺	/	⧺	/	
	Teflon	–	–	–	–	–	–	
	Vinyl chloride	–	+	–	⧺	–	±	Surface blackening
	Urethane	–	±	–	–	±	⧺	Slight bending
Rubbers	Natural rubber	–	–	–	–	+	⧺	
	Butyl rubber	–	–	–	–	+	⧺	
	Neoprene rubber	–	–	±	+	+	⧺	Loss of surface sheen
	Silicone rubber	–	–	–	–	±	+	Surface whitening
	Fluorinated rubber	–	–	–	–	–	–	

* Exposure stopped after 1 day due to marked deformation
/ Not tested; + Moderate effect; – No effect; ⧺ Significant effect; ± Slight effect

PE, 50 μm PE, 20 μm PP and 40 μm PP), permeability to AIT vapor was investigated as shown in Figure 2. AIT vapor was generated in a closed system and forced into a 5 liter Tedlar bag. After connecting this and a second Tedlar bag to a test apparatus with a pump attached, the gas in the right-hand side of the apparatus was replaced by AIT vapor. The gas was replaced 4 times using the pump to alter the direction of gas flow. Then, after removing both Tedlar bags and connecting the inlet ports with a tube (see Fig. 2(3)), the gas at the inlet and the outlet indicated in Figure 2 was sampled at fixed intervals and AIT vapor concentration was measured by gas chromatography under the conditions listed in Table 2. AIT vapor concentration on the inlet side was varied between three levels through dilution with air.

③ Evaluation via weighing method using laminated films

Diatomaceous earth was impregnated with AIT (100 parts earth to 15 parts AIT, by weight), and 50 g portions of the earth were wrapped separately using the seven packaging materials listed below, left in air, and weighed at intervals.

1) No packaging (control), 2) monolayer PP

Table 5. Permeability of Packaging Materials to AIT Vapor (Dish Method)

Type	Material	Thickness (μm)	Total permeation (g/m^2)	
			24 hours	48 hours
Monolayer films	PET	16	0	0
		25	0	0
	CPP	20	43– 47	110– 115
		30	36– 40	93– 97
		40	28– 32	74– 79
		50	26– 30	68– 72
		60	22– 26	58– 63
	OPP	20	51– 55	111– 115
		40	3– 4	10– 12
	PE	30	270–290	590– 610
		50	60– 67	130– 140
	Nylon	20	23– 27	53– 57
	EVA	80	550– 570	985–1010
Composite films	PP/PE blend	70	25– 29	58– 62
Laminated films	Non-woven fabric laminated with PET	37	48– 52	111– 115
	Wood-free paper laminated with PET	68	30– 34	67– 71
	PE-laminated paper*	14	110–118	228– 236
Paper	Wood-free paper**	65	440–470	790– 820
	Glassine paper	90	20– 21	36– 37

* Basis weight 116.3 g/m^2, ** Basis weight 55 g/m^2

(250 μm perforations), 3) monolayer PP (100 μm perforations), 4) paper laminated with PP (450 μm perforations), 5) rayon/15 μm PE/9 μm PET/20 μm PE (130 μm perforations), 6) non-woven fabric/15 μm PE (unperforated), 7) non-woven fabric/30 μm PE (unperforated).

Results and Discussion

1. Corrosion Test

Data regarding the corrosive effect of AIT on the various materials tested is presented in Tables 3 and 4. The results can be summarized as follows:

1) Metals showed no appreciable corrosion, regardless of the concentration of the exposure.

2) Nearly all plastics showed no appreciable corrosion on exposure to 100 ppm. Softening and deformation occurred on exposure to 3,000 ppm in all except polyethylene (PE), polypropylene (PP), nylon (PA6), polyacetal (POM) and Teflon.

3) None of the rubbers, except neoprene exposed to 3,000 ppm, showed any change in external appearance. However, absorption was detected in all except fluorinated rubber.

The experiment thus demonstrated that AIT vapor does not corrode the polyolefin plastic resins widely used in food packaging and could therefore be used in the antimicrobial treatment of foodstuffs wrapped in these films.

Under the conditions established here, contact with the vapor did not cause the reaction in copper reported in the Japanese Food Additive Standards. Nevertheless, in view of the possibility of condensation forming in pipe distribution systems, the most suitable materials for use in an AIT vapor producing device would probably be stainless steel for metal parts and Teflon for

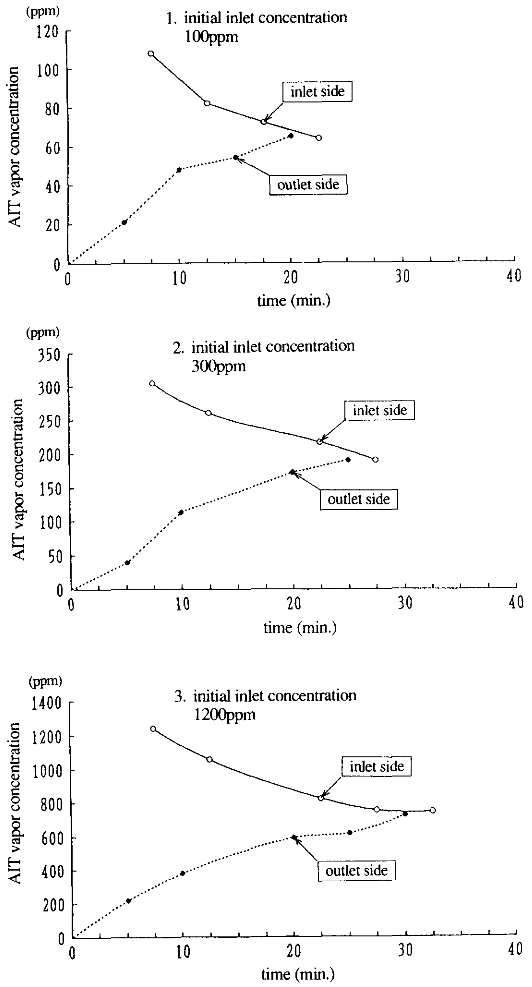

Fig. 3. Permeability of 20 μm PE to AIT vapor

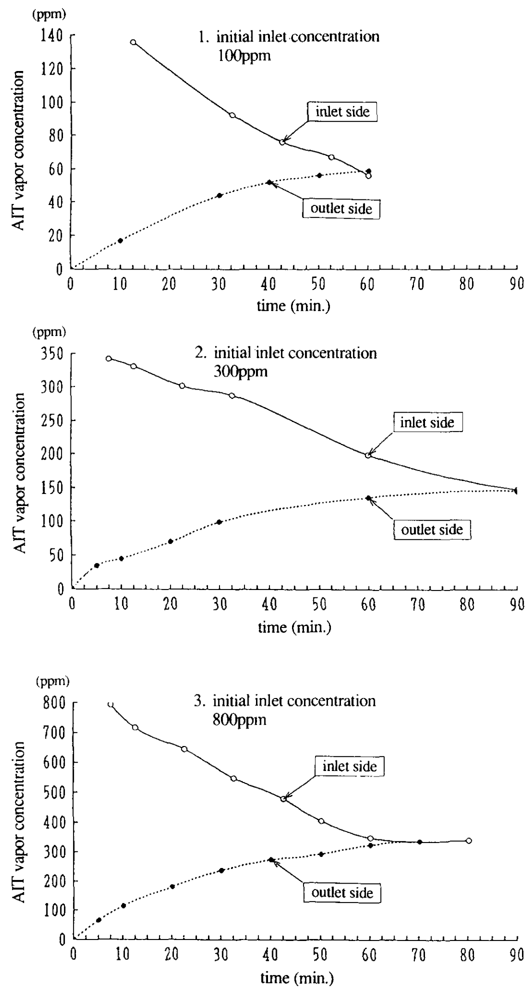

Fig. 4. Permeability of 50 μm PE to AIT vapor

packing.

2. Permeability Test

① Permeability of packaging materials (Dish Method)

Experimental results are shown in Table 5. In descending order of permeability to AIT vapor, the monolayer films ranked thus: EVA>PE>CPP>OPP>nylon>PET, with the latter showing no permeation by AIT even after 48 hours. In an experiment using PE, CPP and OPP of various thicknesses, permeability was found to be inversely proportional to thickness. Of the other materials, the PE/PP blend film, the non-woven fabric and the wood-free paper laminated with PET all showed almost the same permeability as CPP. Of the papers, wood-free paper showed almost the same permeability as EVA, while glassine paper showed almost the same permeability as nylon. There have been many reports[4),5)] on the permeability of these films to gases such as oxygen, water vapor and carbon dioxide. In our experiments, the permeability of the films tested to AIT vapor tended to be similar to their permeability to carbon dioxide.

② Permeability of PE and PP film (special apparatus)

Experimental results are given in Figures 3–6. Using PE and a high AIT vapor concentration of about 1,000 ppm, it took around 30 minutes with 20 μm film and around 60 minutes with 50 μm film for the AIT concentration to reach

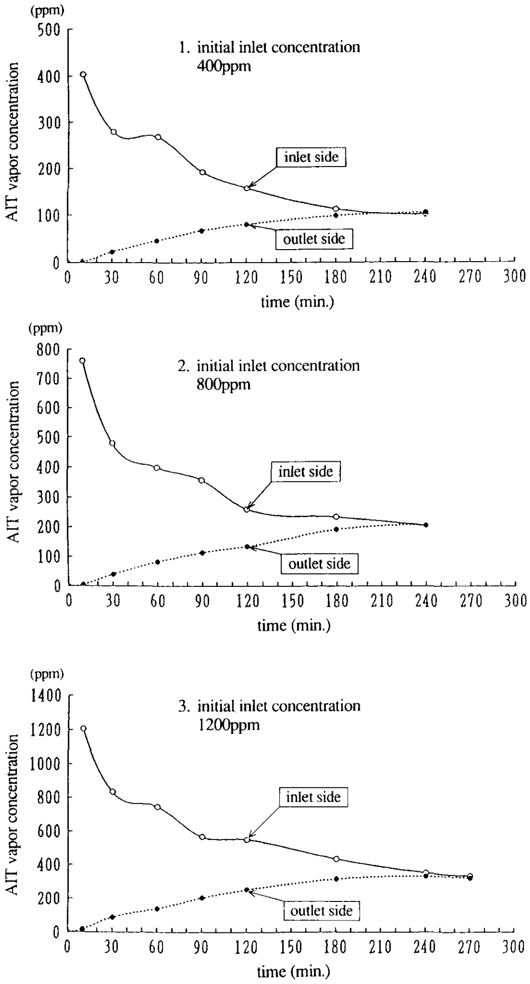

Fig. 5. Permeability of 20 μm PP to AIT vapor

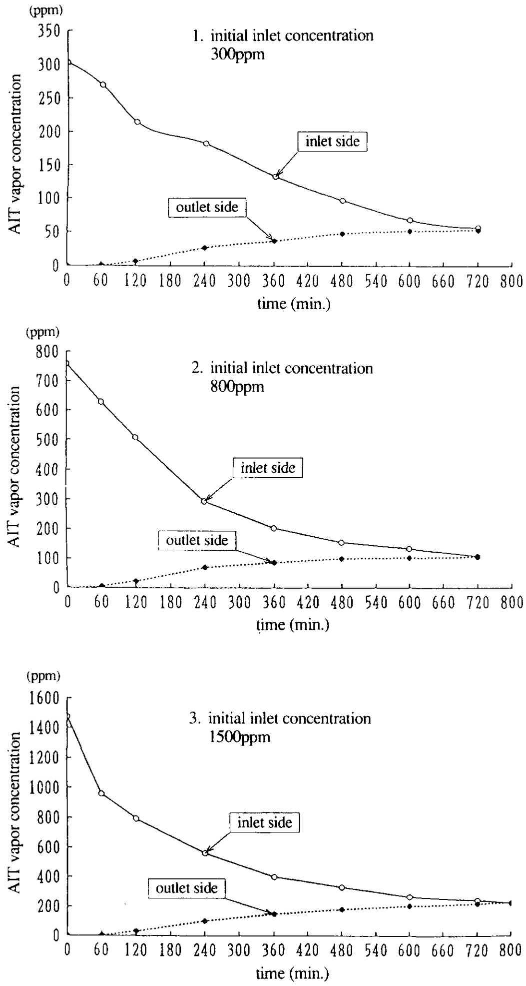

Fig. 6. Permeability of 40 μm PP to AIT vapor

almost the same level on the outlet side as on the inlet side. The equilibrium concentration was approximately half the initial concentration on the inlet side. Using PP and the lowest AIT concentration of 300–400 ppm, equilibrium was reached in around 4 hours with 20 μm film and around 12 hours with 40 μm film. The equilibrium concentration was 1/5–1/4 of the initial inlet concentration, suggesting that absorption by the film took place.

③ Permeability of laminated films (weighing method)

Weight change results for the AIT-impregnated diatomaceous earth samples wrapped in the 6 kinds of laminated film and for the unwrapped control are presented in Figure 7. The monolayer perforated PP film released the AIT at the same rate as the control, and after 50–60 hours almost all the AIT had been lost. In the case of non-woven fabric laminated with unperforated PE, on the other hand, 15 μm film led to the loss of only about 60%, and 30 μm film only about 40% of the impregnated AIT after 100 hours, the time of the last measurement. PP-laminated film conserved almost 80% of the impregnated volume after 100 hours, while rayon-based film showed hardly any loss.

With the increasing importance attached in recent years to maintaining the freshness of foodstuffs, much attention has been given to the use with perishable foods of functional packaging materials, such as those employing anti-

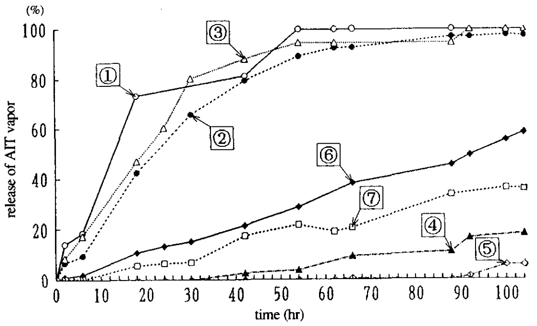

Fig. 7. Permeability of laminated film to AIT vapor evaluated by weighing method
① control; ② monolayer PP (250 μm perforations); ③ monolayer PP (100 μm perforations); ④ paper laminated with PP (450 μm perforations); ⑤ rayon /15 μm PE/9 μm PET/20 μm PE (130 μm perforations); ⑥ non-woven fabric/15 μm PE (unperforated); ⑦ non-woven fabric/ 30 μm PE (unperforated)

microbial agents, and particularly natural antimicrobial agents. It is possible to incorporate inorganic antimicrobial agents such as silver ions or zeolite into plastic resins, and the practical use of such films is already well-advanced[6].

However, the manufacture of films involving treatment with volatile compounds such as AIT and alcohol, which are liquids with high room-temperature vapor pressures, is a very difficult process[7]. The difficulty of incorporating AIT into plastics produced at high temperatures is compounded by the fact, reported in the authors' last paper[1], that AIT disintegrates rapidly at temperatures above its boiling point (170–180℃). Thus, in order to use AIT vapor in the antimicrobial treatment of foodstuffs wrapped in these plastics, the vapor must either be introduced from a source substance inside the wrapping, or be introduced from the outside by permeation through the plastic film. In the former case, to avoid residual odor, the AIT must gradually escape through the wrapping, while in the latter case the AIT must penetrate the wrapping from outside. In either case, therefore, a film using as its main layer PE or PP, which have high AIT vapor permeability, would seem appropriate. There are, of course, a number of factors such as food type and consumption limit which would affect the choice of an optimum combination of wrapping film and AIT vapor source material.

Acknowledgments

We would like to thank Mr. Kazuya Kato of Lintec Corporation Research Laboratory for performing the experiments in which the Dish Method was used to evaluate permeability to AIT vapor.

References

1) Sekiyama, Y., Mizukami, Y., Takada, A., Numata, S.: J. Food Hyg. Soc. Japan **35**, 365–370 (1994).
2) Japanese Ministry of Public Health and Welfare: Food Additive Standards, 6th Ed. p. D-125 (1992), Japanese Food Additive Association.
3) JIS Z 0208, 651–653 (1976).
4) Japan Packaging Technology Society ed.: Packaging Technology Manual, p. 1525 (1988).
5) Watanabe, H.: Food Packaging, **3**, 46 (1988).
6) Hasegawa, H.: Packaging Technology, **25**, 563 (1987).
7) Shinada, R.: Technology for Food Preservation and Storage, p. 314–327 (1988).