**Low temperature-dependence of
N,N-dimethyl-3-methylbenzamide (DEET) release from a
functional paper containing paraffin–DEET composites
prepared using interfacial polymerization**

Hideaki Ichiura^{}, Ken-ichi Yamamoto and Yoshito Ohtani*

Faculty of Agriculture, Kochi University, 200 Monobe-Otsu, Nankoku, Kochi
783-8502, Japan. E-mail: iciura@kochi-u.ac.jp; Fax: +81-88-864-5142; Tel.:
+81-864-5142

**Corresponding author. Faculty of Agriculture, Kochi University, 200 Monobe-Otsu,
Nankoku, Kochi 783-8502, Japan. E-mail: iciura@kochi-u.ac.jp; Fax:
+81-88-864-5142; Tel.: +81-864-5142*

ABSTRACT

An interfacial polymerization reaction was used to prepare a functional paper with a polyamide film containing paraffin–N,N-dimethyl-3-methylbenzamide (DEET) composites, which gave a sustained release of DEET with a low temperature dependence. Preparing the polyamide film using an interfacial polymerization reaction eliminated the need for preparing microcapsules and coating the paper with a binder, which is the typical functional paper preparation method. Filter paper impregnated with an oil–water emulsion (composed of ethylenediamine and paraffin microcapsules prepared using methyl methacrylate polymer) was left in a beaker containing a cyclohexane solution of terephthaloyl chloride. The polyamide film containing paraffin–DEET composites could attach itself to the treated paper surface. We studied the release of DEET from the paper with and without paraffin, and its temperature dependence. The functional paper with paraffin showed the sustained release of DEET at high temperatures, but the release was usually inefficient. However, the sustained release of DEET was not temperature dependent, and this was found to be caused by the release of DEET being controlled by the paraffin melting. The optimum paraffin/DEET ratio was 9:1, taking into consideration the amount of DEET released from the paper and the low temperature dependence of the sustained release of DEET.

Key words: Paraffin, Functional paper, Interfacial polymerization, Low temperature dependence, Sustained release

1. Introduction

Microcapsules are useful for the long-term protection of functional materials from environmental factors, for controlling the release of specific materials, and for converting liquids into the solid state [1–3]. We have studied functional papers, which make use of the native properties of the materials they are made with, and these materials can include adsorbents, antimicrobial agents, and conductive materials [4–12]. Functional papers that release fragrances are useful in applications such as insecticide sheets [12,13], which can release, for example, the insect repellent N,N-dimethyl-3-methylbenzamide (DEET) [14–17], which is the focus of the work presented here. DEET is a popular insect repellent because of its high efficiency and safety. Materials containing DEET are applied to products to repel biting insects. Successful application in our study was defined as the treated paper providing the long-lasting release of DEET.

We have recently investigated fixing functional materials without either microencapsulation or binder-coating processes [12,13,18–22], including preparing functional paper using interfacial polymerization on the paper surface [12,19–21]. This technique will be useful for preparing functional papers that emit DEET. In a previous paper [12], we described the preparation of a polyamide film containing a volatile essential oil (VEO) on the surface of a filter paper using an interfacial polymerization reaction between ethylenediamine (EDA) and terephthaloyl chloride (TC) at the oil–water interface. The residual VEO concentrations in the paper prepared were higher after 96 h than the VEO concentrations in blank paper. This indicated that the VEO was released in a sustained manner. However, the amounts of VEO released from the paper, or the residual VEO in the paper, changed dramatically depending on the ambient

temperature. In other words, the amount of VEO released from the paper increased with increasing temperature, and the amount of residual VEO in the paper at a specific time decreased with increasing temperature. The release of DEET from a functional paper will need to have a low temperature dependence to achieve the efficient and consistent release of DEET over a long period. Therefore, we attempted to prepare a functional paper that would release DEET with a low temperature dependence by incorporating paraffin.

Paraffin with a solid–liquid phase change at a specific temperature has been widely used as a phase change material, and it has been used for thermal energy storage because of its large heat storage capacity, good thermal characteristics, low vapor pressure when melted, and chemical stability [23–26]. Paraffin is in the solid state below its melting point, and it is in the liquid state above its melting point. In the study presented here, we prepared functional paper containing paraffin–DEET composites using an interfacial polymerization reaction on the paper surface. The release of DEET from the functional paper will be controlled by the melting of the paraffin in the functional paper containing the paraffin–DEET composites when the temperature is higher than the melting point of the paraffin. The release of DEET from the functional paper can, therefore, be controlled by the paraffin used. The paraffin used in this study is important in achieving the low temperature dependence of the DEET release from the paper.

In the study presented here, the paraffin–DEET composites were encapsulated using a polymer membrane formed from poly (methyl methacrylate) (PMMA) [27] to improve the affinity of the paraffin for the paper [21]. Once this was achieved, the interfacial polymerization technique, which is a polymerization reaction between EDA

and TC on the paper surface, was applied to prepare the functional paper containing the paraffin–DEET composites. This technique allows a polyamide film containing the paraffin–DEET composites on the paper surface to be produced without the need for a binder. The properties of the paper containing the paraffin–DEET composites are presented here, and the optimal conditions for its preparation were determined. We investigated the effect of the paraffin to DEET ratio in the composites on the temperature dependence of DEET release from the paper.

2. Materials and methods

2.1 Materials

Polyoxyethylene sorbitan monolaurate (Tween 20), methyl methacrylate monomer (MMA), 2,2'-azobis(2,4-dimethyl valeronitrile) (V-65), and DEET were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Anhydrous EDA, cyclohexane, and paraffin (m.p. about 42–44 °C) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). TC was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

2.2 Preparation of functional paper with paraffin–DEET composites on the paper surface

V-65 (0.2 g), used as an azo initiator, was dissolved in melted paraffin (0 or 1–9.99 mL) at 60 °C. DEET (0.01–9 mL) and MMA (8 mL) were poured into an aqueous solution of 2.5% (w/w) EDA (15 mL), 1 M NaOH (15 mL), and Tween 20 (0.5 g), which acted as an emulsifier. Table 1 shows the compositions of the mixtures used for each paraffin–DEET composite tested on the functional paper. The paraffin and aqueous

mixtures were mixed together at 500 rpm with a magnetic stirrer for 10 min at 60°C to prepare an oil–water (O/W) emulsion. The paraffin–DEET composites prepared this way became encapsulated within PMMA. Filter papers (No. 2; Toyo Rosi Kaisha Ltd., Tokyo, Japan) were impregnated with the O/W emulsion containing the paraffin–DEET composite microcapsules and then immersed in a cyclohexane solution (10 mL) of TC (0.1 g) at 25 °C for 10 min, then air-dried at room temperature for 12 h. The functional papers containing paraffin–DEET were stored in 50 mL vials at 4 °C.

2.3 Characterization of paraffin–DEET composites on the paper surface

Fourier transform infrared (FT-IR) spectra were measured using an FT-IR-6100 instrument (JASCO Inc., Tokyo, Japan) using attenuated total reflection at a resolution of 4 cm⁻¹ throughout the spectral range (4000–550 cm⁻¹), with an accumulation of 40 scans.

The paper surfaces were analyzed using scanning electron microscopy (SEM; VE-9800 instrument; Keyence Corporation, Osaka, Japan), with an accelerating voltage of 5 kV, after they had been treated with an osmium coating (Neoc-ST; Meiwafoysis Co., Ltd., Tokyo, Japan).

The latent heat of the paraffin in the paper prepared was measured using a differential scanning calorimeter (DSC; DSC3200SA instrument; Bruker AXS K.K., Kanagawa, Japan). The DSC analysis was performed over the temperature range 10–150 °C, with a heating rate of 15 °C/min.

The tensile strength of the paper prepared using the interfacial polymerization method was determined using a tensile tester (STB; A&D Co., Ltd., Tokyo, Japan). The specimens tested were 20 × 30 mm, and the test speed and span distance were 20

mm/min and 20 mm, respectively.

The wet tensile strength of the functional paper containing paraffin–DEET composites was also measured. A functional paper was dipped in distilled water for 1 min, excess water was removed, then the tensile strength was measured immediately using the tensile strength test method described above.

The water contact angle on the functional paper was measured using a static sessile drop at room temperature. The measurements were performed immediately after drops of water had formed on the surface of the functional paper containing paraffin–DEET composites, using a DM-500 instrument (Kyowa Interface Science Co., Ltd., Saitama, Japan). The contact angle was recorded after 1 s.

2.4 Evaluating the amount of DEET fixed onto the paper

The amount of DEET fixed to the functional paper was evaluated immediately after the paper was prepared.

The DEET in a prepared paper was extracted by immersing the paper in ethanol (3 mL) and placing it in an ultrasonication instrument for 5 min. The solution was filtered through a membrane filter and the DEET concentration in a 1 μ L aliquot was analyzed by high performance liquid chromatography (HPLC; LC-20AD instrument; Shimadzu Corporation, Kyoto, Japan) without further purification. The HPLC instrument was equipped with a C₁₈ column (Kinetex 2.6 μ m C18, 150 mm long, 4.6 mm id; Phenomenex, Torrance, CA, USA) and a UV detector (recording the absorbance at 254 nm). The mobile phase was 70% (v/v) acetonitrile and 30% (v/v) distilled water, and it was used at a constant flow rate of 1.0 mL/min. The column temperature was 40 °C.

2.5 Evaluating the temperature dependence of DEET release from the paper

The release of DEET from the functional paper was evaluated immediately after the paper was prepared.

A prepared paper was placed in a 50 mL vial containing the silica-based MonoTrap™ absorbent (Rcc 18; GL Sciences Co., Ltd., Tokyo, Japan), and the vial was sealed with a silicon septum. The vials were kept for 24 h at either 30 or 50 °C, and the DEET released from the prepared paper during that period was collected by the MonoTrap, which was then extracted by immersing it in ethanol (1 mL) and placing it in an ultrasonic instrument for 5 min at room temperature. The DEET concentration in the extract was determined by HPLC using the same conditions as given above.

Paper samples were also left for 24–72 hours at either 30 or 50 °C, then the residual DEET in the paper was extracted by immersing it in ethanol (3 mL) and placing it in an ultrasonic instrument for 5 min at room temperature. The DEET concentration in the extract was determined by HPLC using the same conditions as given above.

The temperature dependence of the DEET release from a paper containing paraffin–DEET composites was calculated as the release index (REL), and the residual DEET in the paper was calculated as the residual index (RES), as shown in the equations below.

$$REL = (REL_{50} - REL_{30})/R_0 \times 10^3,$$

$$RES = RES_{50} - RES_{30},$$

where REL_{50} and REL_{30} ($\mu\text{g}/\text{m}^2$) are the amounts of DEET released from the paper surface after 24 h at 50 and 30 °C, respectively, R_0 (mg/m^2) is the initial amount of

DEET fixed onto the paper, and RES_{50} and RES_{30} (%) are the amounts of residual DEET in the paper, expressed as percentages of R_0 , after the paper had been stored at 50 and 30 °C, respectively, for 24, 48, or 72 h.

2.6 Preparation of blank paraffin–DEET composites

Blank paraffin–DEET composites were prepared by mixing paraffin (0–10 mL) and DEET (0.01 mL) with a magnetic stirrer at 500 rpm for 10 min at 60 °C, then cooling the mixture to 4 °C. The release of DEET from the blank paraffin–DEET composites was evaluated using the method described above.

3. Results and discussion

3.1 Characteristics of the functional paper containing the paraffin–DEET composites on the paper surface

Fig. 1 shows a FT-IR spectrum of a filter paper after the interfacial polymerization treatment. Cellulose peaks (C–O and C–O–C stretching vibrations) attributed to the filter paper pulp were found at 1200–900 cm^{-1} , as shown in Fig. 1a. The functional paper containing the paraffin–DEET composites prepared using the interfacial polymerization technique showed three characteristic peaks at around 1630 cm^{-1} , attributed to C=O stretching, N–H bending at around 1542 cm^{-1} , and C–N stretching at around 1286 cm^{-1} , the last two being attributed to a C–N–H bond, as shown in Fig. 1b [28]. These peaks were also observed in a polyamide film prepared using the same reaction conditions, which was used as a control for comparing with the paper surface modified using the interfacial polymerization treatment (Fig. 1c), so the peaks were attributed to the polyamide film. The cellulose peaks at 1200–900 cm^{-1} were not present

in the paper after the interfacial polymerization treatment (Fig. 1b). This showed that a polyamide film was formed on the paper surface using the interfacial polymerization treatment.

The tensile strength of the paper before the interfacial polymerization treatment was 2.8 kN/m. The tensile strength of the paper containing paraffin–DEET composites, after the treatment, was 1.8 kN/m. The tensile strength of the paper containing paraffin–DEET composites treated by interfacial polymerization was, therefore, slightly lower than the tensile strength of the blank paper, and this was attributed to the cellulose fiber strength decreasing because hydrogen bonds were destroyed by the EDA solution [29]. However, the paper treated with the interfacial polymerization method was strong enough to handle.

A paraffin peak at around 50 °C (Fig. 2c) was found in the DSC thermogram of the functional paper containing paraffin–DEET composites (Fig. 2b), proving that the paraffin could fix onto the paper surface. The paraffin peak was not observed in the blank filter paper (Fig. 2a). These results show that a polyamide film, including the paraffin–DEET composites, formed directly on the paper surface without the use of a binder.

The wet tensile strength of the functional paper containing paraffin–DEET composites increased as the amount of paraffin in the paper increased (Table S1). The hydrophobicity of the paraffin fixed to the functional paper would have prevented the hydrogen bonds being destroyed by water. The water contact angle with the paper containing paraffin–DEET composites also increased as the amount of paraffin in the paper increased (Fig. S1), and this would have been because increasing the amount of paraffin in the paper will increase the hydrophobicity of the paper. The fixation of the

paraffin onto the paper was demonstrated, and these results show that the functional paper containing paraffin–DEET composites had a lower ability to filter than did the blank filter paper.

The formation of the polyamide film, containing paraffin–DEET composites, on the paper surface using the interfacial polymerization method was confirmed by SEM (Fig. 3b). Fig. 3c shows that the polyamide film containing the paraffin–DEET composites, with microcapsule morphologies, formed using the interfacial polymerization technique were fixed on the paper surface. Cross-sectional SEM images of the polyamide film (Fig. 3d and e) show that the film only formed on the paper surface. The polyamide film was about 2.4 μm thick and had a porous structure (Fig. 3e).

In our previous paper [20], fixing a polyamide film onto a paper surface was shown to become difficult when the polyamide film formed on the paper surface by interfacial polymerization reached about 25 μm thick. These results suggest that the bond between the polyamide film and the paper surface is mainly caused by physical (rather than chemical) bonds. The polyamide film on the paper surface was formed by the reaction between the amino group in the EDA adsorbed onto the paper by physical bonds (causing the coating to form on the paper) and the carbonyl group of the TC. The polyamide film is thought to be fixed to the paper by physical bonds between the paper and the EDA and chemical bonds between EDA and TC [12,19–21].

The performance of the functional paper prepared in this study was maintained for three weeks when the paper was stored at 4 °C in a sealed vial.

3.2 Temperature dependence of DEET release from the functional paper containing paraffin–DEET composites

Table S2 shows the R_0 , REL_{50} , and REL_{30} values for the functional paper containing paraffin–DEET composites and the blank paper without paraffin. The REL_{50} s were significantly higher than the REL_{30} s for the blank paper without paraffin. The differences between the REL_{30} s and REL_{50} s were lower for the functional paper containing paraffin than for the blank paper without paraffin, and decreased as the ratio of paraffin used in the functional paper increased. The REL values were calculated from the REL_{50} , REL_{30} , and R_0 values. Fig. 4 shows the effects of the preparation conditions on the REL values. The release of DEET from the functional paper had a low temperature dependence when the REL value was low, meaning that the sustained release of DEET from the paper was not affected by the temperature. The REL values for the functional papers P 1, P 5, P 9, P 9.9, and P 9.99 were 2.25, 2.77, 3.13, 2.69, and –0.04, respectively. It can be seen that the REL values for the functional papers P 1 to P 9.9 were almost constant, but that the REL value for the functional paper P 9.99 was dramatically lower. The REL values for the blank papers (without paraffin) B 1, B 5, B 9, B 9.9, and B 9.99 were 3.93, 4.26, 7.52, 11.17, and 16.90, respectively. It can be seen that the REL values for the blank papers without paraffin were higher than the REL values for the functional papers with paraffin at the same initial DEET concentration. These results demonstrate that the sustained release of DEET from the functional paper containing paraffin–DEET composites had a low temperature dependence.

Fig. 5 shows the temporal changes in the RES_{50} and RES_{30} values for the functional paper with paraffin and the blank paper without paraffin. The temporal changes in the RES_{50} and RES_{30} values for the functional paper with paraffin both followed the same trend (Fig. 5a). However, the RES_{50} values for the paper without paraffin decreased at a faster rate than the RES_{30} did (Fig. 5b). Table S3 shows the RES_{50} and RES_{30} values for

the paper containing paraffin–DEET composites and the blank paper without paraffin after 72 h. The RES_{50} values for the paper without paraffin were significantly higher than the RES_{30} values. The difference between the RES_{50} and RES_{30} values for the paper containing paraffin decreased as the amount of paraffin used increased. The RES values were calculated from the RES_{50} and RES_{30} values after 72 h. Fig. 6 shows the effects of the preparations used on the RES values. The functional paper gave longer lasting DEET release when the RES values were lower, even if the ambient temperature was high, and the release of DEET had a low temperature dependence. The RES values for the functional papers P 1, P 5, P 9, P 9.9, and P 9.99 were 37.24, 23.91, 5.77, 4.56, and 1.44, respectively. It can be seen that the RES values decreased as the amount of paraffin used increased. The RES values for the blank papers (without paraffin) B 1, B 5, B 9, B 9.9, and B 9.99 were 37.71, 40.36, 37.61, 38.51, and 31.12, respectively. It can be seen that the RES values for the blank papers without paraffin were high for all of the papers prepared, and were higher than the RES values for the functional papers containing paraffin at the same initial DEET concentrations. This shows that the release of DEET from the functional paper containing paraffin–DEET composites had a low temperature dependence, and that the release of DEET was consistent and sustained regardless of the ambient temperature.

The amount of DEET released from the functional paper containing the paraffin–DEET composites was kept low when the paraffin in the functional paper was melted at 50 °C (Fig. 7a). At this temperature the release of DEET from the functional paper containing paraffin–DEET composites was constant and ‘controlled’. The amount of DEET released from the blank paraffin–DEET composites after 24 h at 50 °C decreased as the amount of paraffin used in the composite increased (Fig. S2). The

differences between the amounts of the DEET released from the blank paraffin–DEET composites at 30 °C and 50 °C also decreased as the amount of paraffin used in the composites increased. These results followed the same trend as was seen for the functional paper containing paraffin–DEET composites. The DEET in the paraffin–DEET composites was thought to be retained by the paraffin when it melted, because the paraffin in the blank paraffin–DEET composites was found to melt at 50 °C. These results suggest that the amount of DEET released from the functional paper containing paraffin–DEET could be controlled by the melting of the paraffin.

However, the amount of DEET released from the blank paper without paraffin significantly increased when the temperature was increased from 30 to 50 °C because paraffin was not included (Fig. 7b). It can be seen that the release of DEET from the blank paper without paraffin was affected by the temperature, whereas the release of DEET from the functional paper with paraffin was not affected by the ambient temperature and had a low temperature dependence.

The optimum functional paper was found to be P 9, from the viewpoint of the sustained release of DEET and the amount of DEET released. The REL value for the functional paper P 9 was almost the same as for the functional papers P 1 and P 5, and the RES value for the paper P 9 was lower than the values for papers P 1 and P 5. Functional paper P 9 could, therefore, provide the sustained release of DEET at a higher rate and with a lower temperature dependence than could papers P 1 and P 5. The REL and RES values were lower for papers P 9.9 and P 9.99 than for paper P9, but papers P 9.9 and P 9.99 released significantly lower amounts of DEET than did the other papers. The RES₃₀ values for papers P 9.9 and P 9.99 after 72 h were also lower than the values for the other functional papers tested, as is shown in Table S3. We think that the DEET

in the functional papers P 9.9 and P 9.99 was mainly fixed in the outer polyamide film because the amount of paraffin used in preparing these papers was large, so the DEET was not fixed in the paraffin–DEET composites.

The results may be different at higher temperatures because the paraffin with a melting point of 42–44 °C was used in this study. For practical applications, the paraffin with the optimal melting point will be select for the environment in which it will be used.

The two impregnation processes allow the modification of large amounts of paper, for practical applications, using a paper coating machine. The practicality of using the interfacial polymerization process to produce paper for practical applications is currently being investigated.

4. Conclusions

A polyamide film containing paraffin–DEET composites was prepared on the surface of a filter paper using an interfacial polymerization reaction, and the release of DEET from the functional paper had a low temperature dependence. The polyamide film containing the paraffin–DEET composites was about 2.4 μm thick and had a porous cross-sectional structure. REL and RES values were calculated using the amounts of DEET released from the paper and the residual DEET in the paper after a fixed time, respectively, at 50 and 30°C, to evaluate the temperature dependence of the sustained release of DEET from the paper. The sustained release of DEET from the functional paper was independent of the temperature when the REL and RES values were low. The REL and RES values were lower for the functional paper containing paraffin than for the blank paper without paraffin. Therefore, the sustained release of DEET from the functional paper containing paraffin–DEET composites had a low temperature

dependence. In other words, the amount of DEET released from the functional paper and the amount of DEET remaining in the paper were the same at 30 and 50 °C. This was caused by the volatilization of DEET being controlled by the paraffin in the paper melting at the higher temperature. Therefore, the functional paper containing paraffin–DEET composites was able to release DEET in a sustained manner, in contrast with the functional paper without paraffin. The optimum functional paper studied was paper P 9, from the viewpoint of the low temperature dependence of its sustained release of DEET and the amount of DEET released.

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Figure Captions

Fig. 1. FT-IR spectra of (a) a filter paper and (b) a functional paper containing paraffin–DEET composites prepared using interfacial polymerization, (c) a polyamide polymer prepared using interfacial polymerization. Experimental conditions: 2.5% EDA, 8 mL MMA, 5 mL paraffin, 5 mL DEET, and 1% TC.

Fig. 2. Differential scanning calorimetry thermograms of (a) a filter paper, (b) a functional paper containing paraffin–DEET composites prepared using interfacial polymerization, and (c) paraffin. Experimental conditions: 2.5% EDA, 8 mL MMA, 9 mL paraffin, 1 mL DEET, and 1% TC.

Fig. 3. Scanning electron microscopy images of (a) a filter paper, (b) and (c) a functional paper containing paraffin–DEET composites prepared using interfacial polymerization, (d) and (e) cross-sections of a functional paper containing paraffin–DEET composites prepared using interfacial polymerization. Experimental conditions: 2.5% EDA, 8 mL MMA, 5 mL paraffin, 5 mL DEET, and 1% TC.

Fig. 4. REL (see text for formula) of blank paper without paraffin ($\square$) and functional paper containing paraffin–DEET composites ($\bullet$). The amounts of DEET and paraffin used are shown in Table 1.

Fig. 5. Temporal changes in the residual indices RES_{50} ($\blacklozenge$) and RES_{30} ($\blacklozenge$) (see text for formulae) for (a) functional paper P 9 (see Table 1), containing paraffin–DEET composites and (b) blank paper B 9 (see Table 1).

Fig. 6. RES (see text for formula) of blank paper without paraffin ($\square$) and functional paper containing paraffin–DEET composites ($\bullet$). The amounts of DEET and paraffin used are shown in Table 1.

Fig. 7. Schematic of the release of DEET from (a) functional paper containing paraffin–DEET composites and (b) blank paper, at 30 and 50 °C.

Table 1 The amounts of paraffin and DEET used in the functional papers and blank papers tested

Test paper	Paraffin (mL)	DEET (mL)	Blank paper	Paraffin (mL)	DEET (mL)
P 1	1	9	B 1	0	9
P 5	5	5	B 5	0	5
P 9	9	1	B 9	0	1
P 9.9	9.9	0.1	B 9.9	0	0.1
P 9.99	9.99	0.01	B 9.99	0	0.01

Figure 1 Hideaki Ichiura

Figure 2 Hideaki Ichiura

(a)

(b)

(c)

(d)

Polyamide film

Pulp fiber

(e)

Polyamide film

Pulp fiber

Figure 3 Hideaki Ichiura

Figure 4 Hideaki Ichiura

(a)

(b)

Figure 5 Hideaki Ichiura

Figure 6 Hideaki Ichiura

(a)

(b)