J. Environ. Eng. Manage., 17(6), 403-408 (2007)

NOVEL ENVIRONMENTAL FRIENDLY SOAP-BASED FIRE-FIGHTING AGENT

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Key Words: Eco-friendly, soap, surfactant, extinguishing, foam

ABSTRACT

Fire-fighting agent containing surfactants in major proportions allows fire fighters to extinguish a fire much faster than water alone because the agents reduce surface tension of water, and create a superior foam blanket when mixed with air due to the characteristic properties of surfactants. Since the consumption of the agents will grow at an accelerated pace in the future, the environmental risk of the massive use of such agents should be considered.

In this study, we have developed a novel fire-fighting agent with significantly lower environmental risk, consisting of soaps, chelating agent, and diluents. Soaps are the key major components in our fire-fighting agent, and possess very high biodegradability and very low environmental toxicity particularly for aquatic organisms. The compositions of the soaps were selected by examining the foaming properties and the fluidity. The extinction performance of the resultant agent was confirmed as well.

INTRODUCTION

In Japan, the efficient use of water in fire-fighting activity is of increasing importance after the great Kobe earthquake in 1995. Fire-fighting agents containing surfactants in major proportions have been developed to reduce the usage of water. Due to the characteristic properties of surfactants, the agents reduce surface tension of water, and create a superior foam blanket when mixed with air. Thus, it allows fire fighters to extinguish a fire much faster than water alone.

In the United States, a variety of chemicals including fire-fighting agents have been used to aid in the protection of forest resources from the wildland fires (both woodland and grassland fires) since 1930s [1]. The fire-fighting agents are formulations composed principally of surfactants and act by increasing water efficiency. These chemicals are rapidly gaining acceptance as effective and efficient tools in other countries such as Australia [2,3]. Also, in Japan, the Kitakyushu City Fire and Disaster Management Department and Tokyo Fire Department have been using some fire-fighting agents in the urban fire controls since 1999 and 2000, respectively [4].

However, the commercial fire-fighting agents are restricted in use around the river basin because they show significant toxicity against aquatic organisms [5]. Since the consumption of the agents will grow at an accelerated pace in the future, the environmental risk of using massive amounts of such agents should be considered. Therefore possible eco-toxicities of these chemicals should be tested and the fire-fighting agents should be designed from an environmental point of view.

Use of natural surfactants instead of synthetic

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detergents might be the choice for overcoming certain environmental problems. Our studies have previously shown that viability of *Paramecium bursaria* and *Paramecium caudatum* in the presence of eight natural fatty acid salts (sodium and potassium salts of oleate, palmitate, laurate, and myristate) often used as soap (natural surfactants) can be considerably altered depending on the water quality [6,7]. Our group also showed the ecological risk assessment of fatty acid salts using medaka fish (*Oryzias latipes*) in different water conditions [8,9]. These natural fatty acid salts demonstrated low environmental toxicity for aquatic organisms in natural waters containing certain amounts of minerals such as calcium and magnesium ions [6-9]. The tendencies in toxicity of fatty acid salts in both the protozoa and the fish (medaka fish) examined were reportedly almost identical [6-9].

We have developed a novel fire-fighting agent consisting of soaps, a chelating agent, and diluents with significantly lower environmental impacts [10]. Soaps, which are known to be highly biodegradable, are employed as the key major components in our fire-fighting agent. In this study, we determined the best soap composition for the foaming properties and the fluidity, the fire-fighting performance, and the lowered toxicity in living organisms. Consequently, the environmental performance (based on the eco-toxicity assays) was shown to be much greater than that of synthetic-surfactant-based fire-fighting agent (synthetic fire-fighting agent).

MATERIALS AND METHODS

1. Constituents of Soap-based fire-fighting Agent

Soap components, sodium oleate, potassium laurate, potassium palmitate were obtained from Cognis Deutschland GmbH & Co. KG. *N*,*N*-Bis (carboxymethyl) glutamate tetrasodium salt (GLDA) and propylene glycol (PG) were obtained from Chelest Co. and Asahi Glass Co., Ltd., respectively.

2. Synthetic-surfactant-based Fire-fighting Agent (Commercial Fire-fighting Agent)

The components are alpha-olefin sulfonate solution (60-90 wt%), 2,4-pentanediol (10-30 wt%), 2-methyl-1-dodecanol (1-5 wt%), and d-limonene (1-5 wt%).

3. Pour Point Test

This test was based on Japanese Industrial Standards K 2269 (the pour point test method). Figure 1 shows the diagram of apparatus for measuring the pour point. Ice, sodium chloride, and dry ice were used to lower the cooling bath temperature. 45 mL of the sample (fire-fighting agent) was poured up to the test tube's marker height and was sealed. The test tube was installed in the outer tube and warmed up to 45 °C. The sample was retained for 5 s at the preset temperature. The pour point is defined as the temperature at which the sample lost the fluidity.

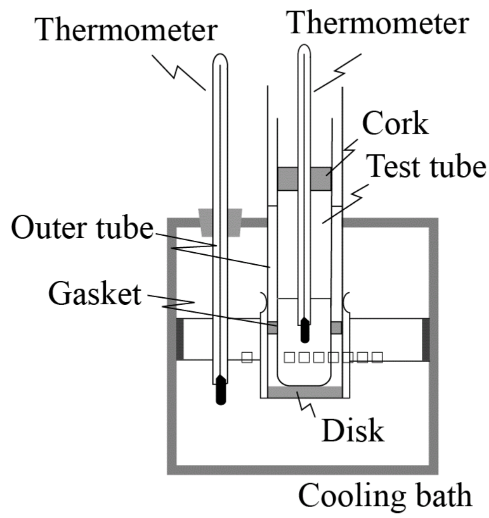

Fig. 1. Apparatus for measuring pour point.

4. Foaming Test

4 L of fire-fighting agent solution at 20 ± 2 °C were sealed into the fire pump (capacity 8 L). Next, nitrogen gas was poured in the fire pump up to 0.85 MPa. The solution was drained off from the fire pump to a bubble collection tank (made of stainless steel, φ 200 mm × h 1.2 m). The steady-state foam height (h, cm) was measured as the distance between the bottom of the tank and the top of the foam. Bubble rate was calculated according to Eq. 1.

$$\text{Bubble rate} = \frac{\text{(foam height)(tank cross} - \text{sectional area)}}{\text{(volume of the aqueous solution)}} \quad (1)$$

5. Fire-fighting Test

82 timbers of Japanese cedar were combined and the combustible, which is called a crib, was prepared (Figs. 2 and 3). Moisture content of the crib was maintained between 10 and 15%. The crib was burned by igniting a 300 mL of heptane poured into the bottom of the pan. The crib was kept burning for 2 min. Then the fire-fighting agent solution was sprayed off around at 15 L min^{-1} from the F1/2EX4100 type nozzle for 10 s, and cut off from supplies for 50 s. The procedure was repeated until the crib burned out or fell off. During the fire-fighting test, the temperature above the crib was measured at 2 s intervals.

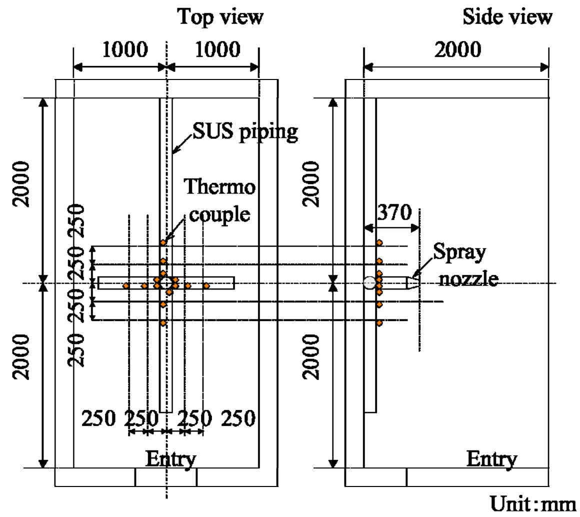

Fig. 2. Apparatus for measuring fire test.

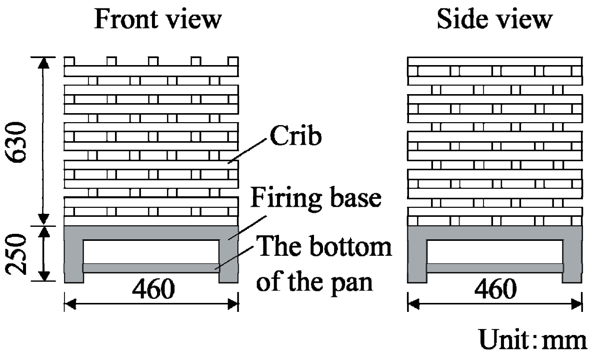

Fig. 3. Construction drawing of the crib.

6. Organism for Toxicity Assay

The *P. bursaria* strain F1-1b and the *P. caudatum* strain SIO-2 were used according to the previous paper [6,7]. The primary culture of SIO-2 and F1-1b were propagated in the medium made up of a yeast extract-based nutrition mixture EBIOS (1 tablet L^{-1}; Asahi food & Healthcare, Tokyo), after inoculation with the food bacterium *Klebsiella pneumoniae*, under a light cycle of 12 h light and 12 h dark with *ca.* 3500 lux of natural-white fluorescent light at 23 °C as described previously [6,7]. The bacterized medium was prepared by inoculating the medium with *K. pneumoniae* one day prior to inoculation with ciliate cells. For toxicity tests, different waters (see below) were used for preparing the EBIOS media. Prior to preparation of the EBIOS medium, dechlorination of tap waters (TW) were carried out by autoclaving (121 °C, 20 min).

Two different waters, namely distilled water (DW) and Kitakyushu city TW originated from the Onga river, were used for preparation of the EBIOS media.

7. Toxicity Assay

For toxicity assays, paramecia in the stationary phase were washed once with the EBIOS medium made up of ultra-pure water and then washed twice with the EBIOS media made up of different waters to be used. The tests with *P. bursaria* and *P. caudatum* were carried out on 12-well microplates. Each well on the plates was filled with 0.9 mL of EBIOS media harboring 100 paramecium cells plus 0.1 mL of detergent solutions. Then the cells were incubated for 12 h at 23 °C under continuous dark conditions, and the number of living cells was counted at the end of the incubation under a stereomicroscope (SMZ645; Nikon, Tokyo).

RESULTS AND DISCUSSION

1. Selection of Constituents

Sodium oleate, potassium laurate, and potassium palmitate were employed as soap components since they are well known to enhance the wettability, the foaming property, and the foam stability of aqueous solution. Soap combines easily with minerals such as calcium and magnesium ions in TW. It is also able to lose the interfacial activity immediately. Chelating agents should be added in a soap-based fire-fighting agent to inhibit the soap-mineral complex formation in TW. GLDA possessing an amino acid backbone was selected as a chelating agent because of its better biodegradation behavior. Diluents containing PG and pure water were added to maintain the fluidity of the agent.

Previously, our group evaluated for assessing the acute toxicity of eight fatty acid salts (sodium and potassium salts of oleate, laurate, and palmitate) using green paramecia (*P. bursaria*) and *P. caudatum* under various water conditions [6,7]. In the low mineral culture medium prepared with DW, the median lethal concentration (LC_{50}) for each fatty acid ranged from 5.8 to 144 ppm (w/v). The toxic levels of fatty acid salts differed in the following order: laurate ≥ oleate, palmitate. The toxic levels of oleate and palmitate salts were *ca.* 10-fold lower than those of laurate salt. When river water and local TW were used for culturing instead of ultra-pure water, the toxic levels of all fatty acid salts were drastically lowered compared to the low mineral condition by 30- to 100-fold (198-660 ppm w/v). Similar detoxification effects were observed when Ca or Mg was added to the low mineral culture media, indicating that the toxicity of fatty acid salts can be notably lowered as the mineral content increases. The toxicity of GLDA is equal to the toxic levels of oleate and palmitate salts. Surprisingly, the toxicity was decreased when GLDA and laurate salt coexist. Other constituents have also low toxicity to green paramecia.

Toxicity assay of each constituent showed that laurate salts have the highest toxicity among the components. Therefore, to improve environmental performance, it could be important to reduce the amount of laurate salts.

2. Composition Ratio of Fatty Acid Salts

When water is discharged to burning materials, most water flows out and contributes little in extinguishing a fire because of its high surface tension. Fire-fighting agent containing surfactants reduces the water surface tension and induces foam formation. The water can stay around the burning materials for a long time and fulfill its role as an extinguisher. Therefore, the wettability, foaming property, and foam stability are required for fire-fighting agent. From the results of preliminary experiments, the foaming property is found to correlate strongly with the extinction performance. The fluidity of fire-fighting agent is also important so that it is available even in cold season. The bubble rate and the pour point are useful indicators for the foaming property and the fluidity. At 0.5 wt% aqueous solution with a synthetic commercial fire-fighting agent, the bubble rate and the pour point are 5.0 and -5.0 °C, respectively. Thus we set these values as the target values in development of fire-fighting agent.

Bubble rate and pour point were measured for the fire-fighting agent containing soaps, diluents, a chelating agent. Here, the percentage of fatty acid salt, chelating agent, and diluents are 14.0, 33.4 and 52.6 wt%, respectively.

The relative proportion of sodium oleate and potassium laurate was determined from the results of the foaming test and the pour point test. The bubble rate decreased when the ratio of sodium oleate exceeded 60% at 1.5 vol% of the fire-fighting agent solution (Fig. 4a). Meanwhile, the pour point has the lowest value at 60% of sodium oleate (Fig. 4b). Therefore, the mixture ratio of sodium oleate and potassium laurate was determined to be 60:40. As the results of further investigation into the optimum proportion of fatty acid salts, potassium palmitate was added other than sodium oleate and potassium laurate. Finally, the composition of the soap-based fire-fighting agent containing soaps, diluents, and a chelating agent is summarized in Table 1.

3. Fire-fighting Test of the Soap-based Fire-fighting Agent

To examine the extinction performance of the soap-based fire-fighting agent, the fire-fighting test in a model fire was conducted. TW and synthetic fire-fighting agent were also evaluated by the same test.

The temperature above the crib during the fire-fighting test is shown in Fig. 5. Figure 6 demonstrates the snapshots of the burning crib when the soap-based fire-fighting agent or TW was discharged onto the crib. Even after TW was discharged over 5 times, the temperature above the crib was over 200 °C, and the fire in the crib did not burn out. The crib broke down at the last. For the soap-based fire-fighting agent (1.0 vol%) and the synthetic fire-fighting agent (0.5 vol%), the temperature above the crib was under 200 °C after the 3rd time discharge, and the fire in the crib burned out completely before the 5th time discharge.

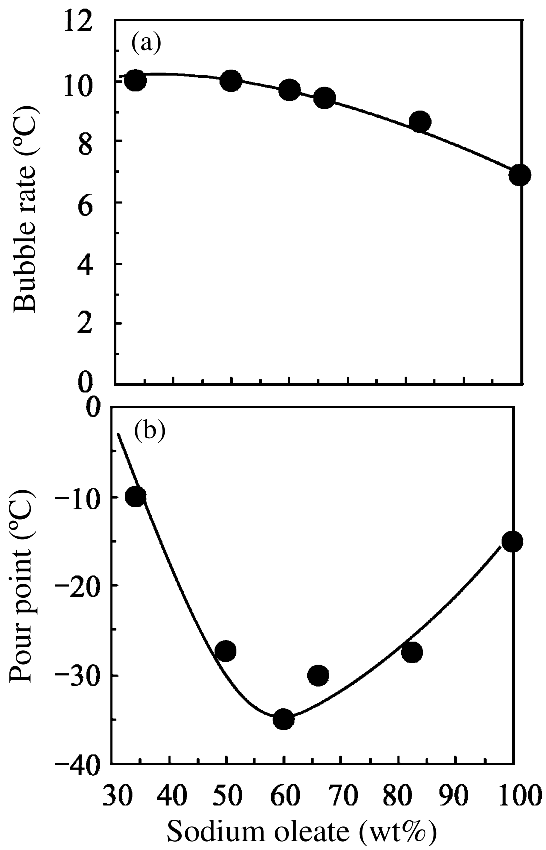

Fig. 4. Relation between (a) bubbe rate and (b) pour point and the ratio of sodium oleate and potassium laurate.

Table 1. The composition of the soap-based fire-fighting agent

Percent composition (wt%)				
Sodium oleate	Potassium laurate	Potassium palmitate	GLDA	Diluents
10.00	6.87	0.10	40.00	43.03

4. Toxicity Assay of the Soap-based and the Synthetic Fire-fighting Agents

We compared the toxicity of the soap-based fire-fighting agent and synthetic fire-fighting agent in *P. caudatum* and *P. bursaria* under DW as low mineral condition and TW as high mineral condition. The culture media themselves prepared from the DW and TW had no lethal effect on the survival of *P. caudatum* and *P. bursaria* in the absence of fire-fighting agents (data not shown). The toxic levels

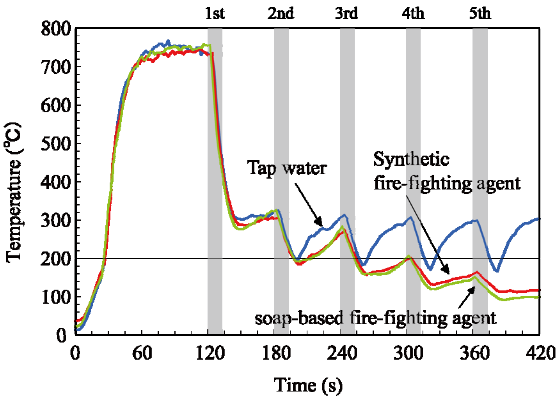

Fig. 5. The extinction performance of tap water, synthetic fire-fighting agent (0.5 vol%), and the soap-based fire-fighting agents (1.0 vol%). Graphs show the change of temperature at the top of crib. Gray zone indicates discharge period.

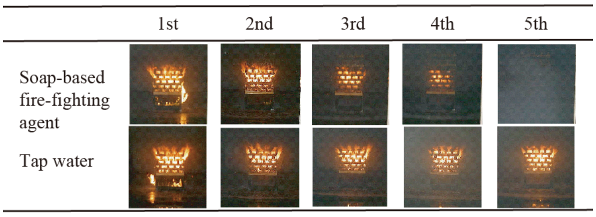

Fig. 6. Snapshots at each discharge of the soap-based fire-fighting agents (1.0 vol%) and tap water.

of the soap-based fire-fighting agent were almost equal to one of synthetic fire-fighting agent under DW. The toxic levels of the soap-based fire-fighting agent were drastically lowered compared to synthetic fire-fighting agent in *P. caudatum* and *P. bursaria* under TW. The toxic levels of the soap-based fire-fighting agent under TW conditions were drastically lowered compared to DW. The lethal concentrations (LC_{100}) of the soap-based fire-fighting agent after 12 h of incubation under TW were 10- to 30-fold lower than those determined under DW. The LC_{50} value for the soap-based fire-fighting agent was also drastically lowered (Table 2). The soap-based fire-fighting agent readily reacts with cations (mainly calcium and magnesium ions) in water, and this results in the formation of insoluble precipitates of metallic soaps which are inert to the biomembranes since the Ca/Mg-replaced metallic soaps no longer possess the surfactant activity. Therefore, the use of tap water is highly encouraged on the eco-toxicity (toxicity assay) impacts of variety of chemicals.

CONCLUSIONS

We have successfully developed a novel soap-based fire-fighting agent with significantly lower environmental risk to reduce the usage of water. The components of this fire-fighting agent were selected

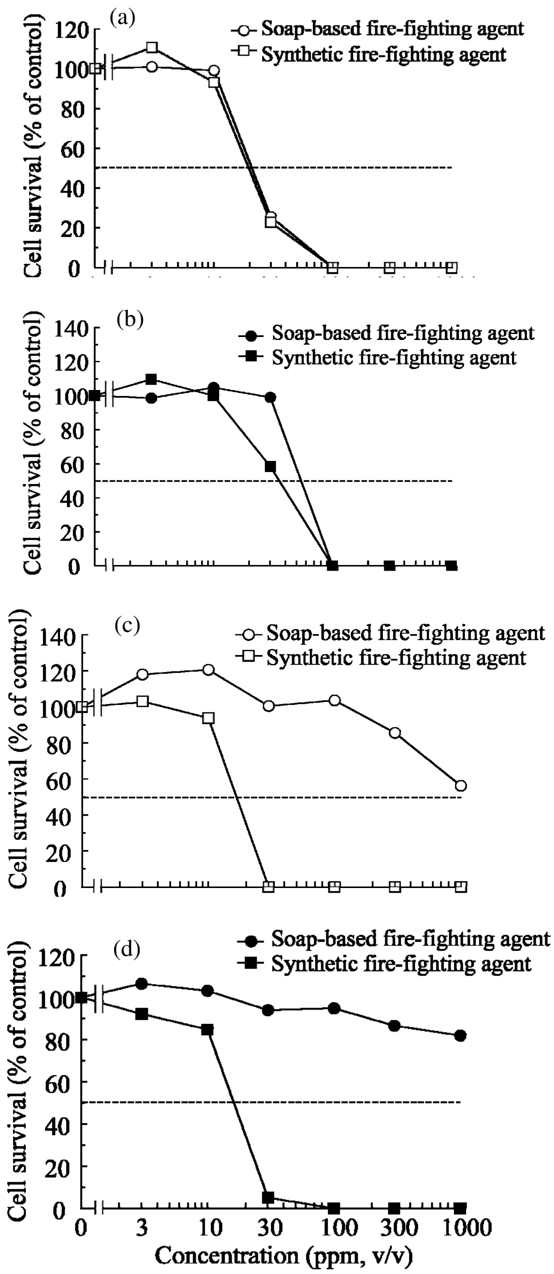

Fig. 7. The toxicity of the soap-based fire-fighting agent and synthetic fire-fighting agent in (a) *P. caudatum* and (b) *P. bursaria* under distilled water (DW) and (c) *P. caudatum* and (d) *P. bursaria* under tap water (TW). Graphs show the cell survival rates after 12 h of exposure to each fire-fighting foams.

by examining the foaming properties and the fluidity, and the extinction performance. The fire-fighting agents consist of the following: soap components (sodium oleate, potassium laurate, and potassium palmitate), chelating agent (GLDA), and diluents. The novel soap-based fire-fighting agent (1.0 vol%) demonstrates sufficient extinction performance and very-low environmental toxicity for aquatic organism com-

Table 2. The LC_{50} and LC_{100} values (ppm) for synthetic fire-fighting agent and soap-based fire-fighting agent determined in *Paramecium bursaria* F1-1b cells and the *Paramecium caudatum* strain SIO-2 cells with distilled water (DW) and tap water (TW)

		Synthetic fire-fighing agent		Soap-based fire-fighting agent	
		P. caudatum	*P. bursaria*	*P. caudatum*	*P. bursaria*
LD_{50}	DW	20	33	23	41~53
	TW	17	17	980~1200	1500~1800
LD_{100}	DW	100	100	100~300	100~300
	TW	30	100	3000	3000

pared to synthetic fire-fighting agent. In addition, the foam lifetime of this fire-fighting agent was shown to be shorter than that of the synthetic fire-fighting agent, thus readily enabling the removal of fire-fighting agent from the flora after a fire-fighting activity (in case of wildland fire). Moreover, in case of urban fires, the fire-fighting agent with short foam life allows the on-site investigation by fire department officers or police to be performed much faster soon after a fire-fighting activity at the site of incidence.

ACKNOWLEDGEMENTS

This work was supported by a grant-in-aid from the Fire and Disaster Management Agency of Japan.

REFERENCES

1. USDA Forest Service, Wildland fire suppression. In: Ecological Risk Assessment, Forest Service, United States Department of Agriculture, Washington, D.C. (1994).
2. Rawet, D., R. Smith, and G. Kravainis, A comparison of water additives for mopping-up after forest fires. Int. J. Wildland Fire, 6(1), 37-43 (1996).
3. Adams, R. and D. Simmons, Ecological effects of fire fighting foams and retardants. Proc. Austr. Bushfire Conf. 1999, Albury, Australia (1999).
4. Kitakyushu City Fire and Disaster Management Department, Research and development of ecologically acceptable fire suppression formula for urban fires. Gekkan Shobo (Monthly Fire Fighting by Tokyo Ho-Rei), No. 313, 1-8 (2005). (In *Japanese*)
5. Birnbaum, L.S., Brominated flame retardants: Toxicology and risk. USEPA Emerging Pollutants Workshop, Chicago, IL, Aug. 11-14 (2003).
6. Kawano, T., K. Uezu, T. Kosaka, and T. Kawano, Altered toxicities of fatty acid salts in green paramecia cultured in different waters. Z. Naturforsch. C, 61(7-8), 541-547 (2006).
7. Kadono, T., K. Uezu, and T. Kawano, Confirming the altered toxicities of fatty acid salts in *Paramecium caudatum* cultured in different waters. ITE Lett. Batter. New Technol. Med., 7(6), 606-609 (2006).
8. Lin, C., T. Kadono, K. Yoshizuka, K. Uezu, and T. Kawano, Assessing the eco-toxicity of novel soap-based fire-fighting foam using medaka fish (*Oryzias latipes*, Red-orange variety) adopted to river and sea water conditions. ITE Lett. Batter. New Technol. Med., 7(5), 499-503 (2006).
9. Kawano, T., C. Lin, T. Kadono, and K. Uezu, Ecological risk assessment of fire-fighting chemicals using medaka fish (*Oryzias latipes*) in different water conditions, ITE Lett. Batter. New Technol. Med., 8(3), 306-311 (2007).
10. Uezu, K., Novel environmentally friendly fire-fighting agent. Proc. Japan-Taiwan Joint Int. Symp. Environ. Sci. Technol. Environ. Chem. Biosci. Manag. Kitakyuhsu, Fukuoka, Japan, pp. 36-38 (2007).

Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

Manuscript Received: May 30, 2007
Revision Received: October 6, 2007
and Accepted: October 12, 2007