

1 **Oil-in-water microemulsion containing ferrocene: A new fire suppressant**

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1 **Abstract**

2 This paper reports the preparation and fire-suppression efficiency of oil-in-water microemulsions
3 containing ferrocene. In this work, oil-in-water emulsions containing 0–1,000 ppm ferrocene and four
4 surfactants (Surfynol 465, Olfin E1020, Triton X-100 (TX), and Noigen TDS-80 (NT)) were prepared
5 by homogenizing n-octane solutions of ferrocene and aqueous surfactant solutions at ambient
6 temperature. Four emulsion parameters were then characterized: emulsion stability, oil-droplet size in
7 emulsion, flash point, and capability of extinguishing n-heptane pool fires. Emulsion stability
8 experiments and droplet-size measurements clearly demonstrated that the oil-in-water emulsions
9 containing ferrocene and TX/NT were thermodynamically stable microemulsions. Flash-point
10 measurements confirmed that no oil-in-water microemulsions tested ignited below 93 °C. Suppression
11 trials involving microemulsions containing 0–1,000 ppm ferrocene and NT revealed the relationship
12 between their fire suppression efficiency and the concentrations of ferrocene and NT, and also
13 demonstrated that the microemulsions tested in this study have a higher ability to suppress pool fires
14 compared with a conventional wet chemical agent.

15

16 **Keywords:** Fire suppression; Ferrocene; Oil-in-water microemulsion; Phosphorus free; Fire-
17 extinguishing agent; Water mist; Noigen TDS-80 (Lutensol TO 89); Surfactant; Extinguishment; Pool
18 fire

1

2 **Abbreviations**

3	ANOVA	Analysis of variance
4	Bu	Butyl
5	d	Droplet diameter (nm or μm)
6	F	F value (also called F statistic; dimensionless)
7	FeCp ₂	Ferrocene
8	HA	Height of an aqueous layer (mm)
9	HE	Total height of the emulsion (mm)
10	HMIS	Hazardous Materials Identification System
11	HO	Height of an oil layer (mm)
12	Me	Methyl
13	ME	Microemulsion
14	ME _{NT} (x, y)	Microemulsion containing NT, x -wt% oil, and y -ppm ferrocene
15	ME _{TX} (x, y)	Microemulsion containing TX, x -wt% oil, and y -ppm ferrocene
16	n	Number of droplets (dimensionless)
17	NFPA	National Fire Prevention Association
18	NT	Noigen TDS-80

1	OE	Olfin E1020
2	O/W	Oil-in-water
3	p	Probability, p-value (dimensionless)
4	PS	Phase separation (vol%)
5	R	Weight ratio of n-octane to surfactant (dimensionless)
6	SMD	Sauter mean diameter (nm or μm)
7	SN	Surfynol 465
8	Soln.	Aqueous solution
9	TX	Triton X-100
10	USD	U.S. dollar
11	W	Weight (g)
12		
13	<i>Greek characters</i>	
14	σ	Standard deviation of extinguishing times (s)
15	τ	Average extinguishing time (s)
16		
17	<i>Subscripts</i>	
18	m	Mist

- 1 ME Microemulsion
- 2 NT Noigen TDS-80
- 3 o Oil
- 4 oct n-octane
- 5 surf Surfactant
- 6 TX Triton X-100

7

8 *Superscripts*

9 *i* iso-

10 *t* tert-

11

12 **1. Introduction**

13

14 Accidental fires are disaster that can lead to human suffering, property losses, and environmental
15 damage. Thus, they are an important social issue in most countries; for instance, fires in the United
16 States and Japan still claimed the lives of 3,275 and 1,675 people in 2014, respectively. In many
17 situations, containing and extinguishing a small developing fire with handheld fire extinguishers is of
18 great importance. Developing more effective fire suppressants is, therefore, of considerable help in

1 reducing such fire-related casualties. Nowadays, phosphates and their derivatives are widely used as
2 fire-extinguishing agents [1,2]. As is well known, phosphorus is one of the three major nutrients in
3 crop production. As shown in Fig. 1, owing to recent global problems involving nonrenewable
4 phosphate rock such as future scarcity and dramatically increased costs [3,4], developing not only
5 efficient phosphorus recycling and recovery techniques [5] but also alternatives for phosphorus-based
6 fire suppressants are required at present.

7 Water-mist technology has received increasing attention because of its low-cost, ubiquity, and
8 environmentally friendly properties. It is known that the major mechanisms through which water mist
9 extinguishes fires involve the removal of heat in the flame zone (or fuel surface), attenuation of thermal
10 radiation, and displacement of oxygen [6]. Additives to water are often required to further enhance its
11 suppression capability and these typically include surfactants [7], antifreezes [8], and metallic
12 compounds. Several transition metals have the ability to catalytically scavenge radicals involved in
13 the gas-phase chain reactions. They exhibit various oxidation states, which means that transition-metal
14 compounds can potentially behave as flame inhibitors. Of all the transition-metal compounds,
15 ferrocene (FeCp_2 , Fig. 2a), an organo-iron compound, is a novel promising flame inhibitor due to its
16 high radical-trapping capability [9,10]; ferrocene and its derivatives are applied in related areas as
17 smoke suppressants and flame retardants [11–14]. Despite its excellent extinguishing properties, using
18 ferrocene as an additive in water poses two problems: strong fraction-dependency of fire-suppression

1 efficiency and insolubility in water. The former reflects the fact that the ability to suppress a flame
2 dramatically decreases at lower and higher ferrocene fractions, i.e., an optimum amount of ferrocene
3 must be introduced into a flame. The latter means that it is difficult to directly add ferrocene (as-is) in
4 water because of its high lipophilicity. Koshiha and co-workers reported a ferrocene-containing water-
5 based fire suppressant: aqueous ferrocene dispersions having an optimum ferrocene concentration
6 using dispersion techniques [15,16]. The earlier studies clearly demonstrated that (i) aqueous
7 dispersions containing smaller ferrocene particles exhibit higher dispersibilities and that (ii) the fire-
8 extinguishing capabilities of ferrocene dispersions are positively correlated with their dispersibility.
9 However, they also revealed that the dispersibility steeply decreases in a short time, potentially
10 resulting in a decrease in their suppression ability. In addition, directly dispersing organometallic
11 ferrocene powder in water may cause the ferrocene to degrade, so that ferrocene dispersions eventually
12 break down. To solve these issues, Koshiha and co-workers recently proposed a new ferrocene-
13 containing emulsion-based fire suppressant: a ferrocene-containing emulsion [17]. This emulsion
14 technique involves dissolving ferrocene in oil and then dispersing the solution in an aqueous medium
15 using surfactants. Unfortunately, however, this earlier study only reported one emulsion system.

16 By definition, oil-in-water (O/W) “macroemulsions” are heterogeneous, opaque, and
17 thermodynamically unstable systems in which oil droplets will coalesce, eventually leading to phase
18 separation. In contrast, oil-in-water “microemulsions” have nano-sized oil droplets and are

1 macroscopically homogeneous and thermodynamically stable systems; they also have some
2 distinguishing physicochemical properties: optical transparency, isotropy, and low viscosity [18]. The
3 present work focuses on the fire-suppression capability of ferrocene-containing microemulsions. The
4 major advantages of using microemulsion techniques are as follows:

5

6 ● The dispersibility, which is positively correlated with the suppression capability as stated above,
7 would be dramatically improved if thermodynamically stable ferrocene-containing
8 microemulsions can be formed.

9 ● Oil-in-water microemulsions have nano-sized oil droplets in which molecular ferrocene dissolves.
10 The extinguishing efficiency is typically enhanced as the particle size of a suppressant decreases
11 [19]. Hence, ferrocene-containing microemulsions would have higher extinguishing efficiency
12 compared with aqueous dispersions containing micron-sized ferrocene particles.

13 ● Dissolving organometallic ferrocene in the oil phase may prevent its direct reaction with water
14 and subsequent decomposition.

15

16 The present study aims to prepare new, phosphorus-free, stable n-octane/water microemulsions
17 containing surfactants and ferrocene, and to experimentally elucidate their fire-suppression
18 capabilities. In this study, four surfactants were used: Surfynol 465 (hereafter referred to as SN), Olfin

1 E1020 (OE), Noigen TDS-80 (NT, also known as BASF Lutensol TO 89), and Triton X-100 (TX), as
2 depicted in Fig. 2b–e. These surfactants having low critical micelle concentrations are used in various
3 applications including life-, food-, and material sciences [20–22] because, for instance, Surfynol 465
4 complies with Food and Drug Administration and Environmental Protection Agency regulations and
5 Noigen TSD-80 exhibits high biodegradability. In general, varying the surfactant used in the solution
6 will modify the emulsion stability [23], possibly improving the fire-extinguishing efficiency. The
7 stability of the ferrocene-containing O/W emulsions was determined using a phase separation method
8 [24]. In the suppression experiments, an n-octane/NT/water emulsion system in which no phase
9 separation had occurred was evaluated for its ability to extinguish pool fires.

10

11 **2. Materials and Methods**

12

13 *2.1 Chemicals*

14

15 Ferrocene (purity > 98.0%) was purchased from Sigma-Aldrich Co., USA and used without further
16 purification. Water was used after deionization. To form ferrocene-containing O/W microemulsions,
17 four nonionic surfactants were employed: SN, OE, NT, and TX, as described above. Dry n-octane
18 (purity > 98.0%) was employed because of its high ferrocene solubility at room temperature [17].

1

2 2.2 Emulsion Preparation

3

4 Ferrocene-containing O/W emulsions were prepared by thoroughly homogenizing n-octane
5 solutions of ferrocene and aqueous surfactant solutions at room temperature for 15 min at 5000 rpm
6 using a homogenizer (T18, IKA, USA). When the concentration of n-octane is set to 2.1 wt%, the O/W
7 emulsions can have a ferrocene content of up to 1000 ppm on a mass/mass basis. In this study, the
8 weight ratio of n-octane to the surfactant, R , was varied between $R = 1.0$ and $R = 5.0$ [17].

9

$$10 \quad R = \frac{W_{\text{surf}}}{W_{\text{oct}}} \quad (1)$$

11

12 where W_{surf} and W_{oct} are the weights of the surfactant and n-octane, respectively.

13

14 2.3 Emulsion Characterization

15

16 2.3.1 Emulsion Stability

17 O/W macroemulsions generally exhibit poor stability when used without any amphiphile (e.g.,
18 surfactant). The phase separation of O/W macroemulsions is triggered by several destabilization

1 mechanisms: creaming, sedimentation, flocculation, and Ostwald ripening [25]. Such destabilization
2 causes irreversible coalescence of oil droplets, eventually leading to phase separation. As described
3 previously, emulsion instability would reduce its extinguishing capability; in addition, unstable
4 emulsions may be flammable, since the oil tends to concentrate in the upper layers of the mixture as a
5 result of the density difference between the phases (density of n-octane: $0.70 \text{ g/cm}^3 < \text{density of water:}$
6 1.00 g/cm^3 at $20 \text{ }^\circ\text{C}$). Hence, evaluating emulsion stability is of great importance in this study.

7 Typical techniques for determining emulsion stability include zeta potential, nuclear magnetic
8 resonance, and light scattering methods [26,27]. In this study, the emulsion stability was simply
9 evaluated using the phase separation method [28]. 100 mL of each fresh, uniform emulsion was poured
10 into flat-bottomed glass test tubes (35 mm in diameter and 125 mm in length) so as not to foam, and
11 then the test tubes were capped and conditioned at $25 \text{ }^\circ\text{C}$ in a thermostatic chamber. The gravity-
12 induced phase separation was monitored for a long period (25 months) by measuring the amounts of
13 separated free oil and water phases. The phase separation (*PS*) was determined by the percentage of
14 free oil phase according to Eq. (2).

15

16
$$PS = \frac{100 \cdot HO}{HE} = \frac{100 \cdot HO}{HA + HO}, \quad (2)$$

17

18 where *HE* is the total height of the emulsion, *HO* is the height of the oil layer, and *HA* is the height of

1 the aqueous layer.

2

3 *2.3.2 Emulsion Droplet-Size Distribution*

4 The oil-droplet size in emulsions remarkably affects their appearance, reactivity, rheology, color,
5 and stability [29,30]. Besides these physicochemical properties, the size of oil droplets containing
6 ferrocene probably dominates the fire-extinguishing efficiency due to the particle-size dependency of
7 the suppression ability, as stated above [19]. Hence, it is essential to gain an insight into the oil-droplet
8 size distribution. In this study, the droplet-size distribution of the prepared O/W microemulsions was
9 measured at 25 °C using a dynamic light scattering instrument (ELS-Z 2, Otsuka Electronics, Co. Ltd.,
10 Japan), and the mean oil-droplet size was expressed as the Sauter mean diameter (SMD) by the
11 following equation:

12

$$13 \quad SMD = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}, \quad (3)$$

14

15 where n_i is the measured number of droplets with diameter d_i .

16

17 *2.3.3 Flash-Point Measurements*

18 As described above, the O/W emulsions tested in this study contained n-octane (flash point: 13 °C,

1 [31]). We cannot use the O/W microemulsions as fire suppressants if they are highly flammable at
2 ambient temperature. In this study, the flash points of the O/W emulsions were determined using a
3 Tag closed-cup tester (TAG-E, Yoshida Kagaku Kaisha Co., Ltd., Japan) according to a standard test
4 method [32].

5

6 *2.3.4 Suppression Experiments*

7 Before conducting the suppression trials, the spray droplets, which strongly govern the
8 extinguishing efficiency, were measured using the immersion technique [33]. This method involves
9 gathering spray droplets with an immiscible liquid (e.g., silicone oil), and then directly making
10 microscopic observations of the droplet size (DMI 2000B, Leica, Germany). Note that the droplet size
11 may change depending on the measuring methods, such as phase Doppler, laser diffraction, freezing,
12 photographic, and immersion methods [33]. Nevertheless, as mentioned later, the oil-droplet size of
13 the O/W microemulsions used in this study was three orders of magnitude smaller than the spray
14 droplet, implying that the spray mist probably comprises emulsion droplets.

15 Fig. 3 illustrates the experimental apparatus used for the suppression trials, which was built to
16 simply elucidate the ability to suppress pool fires. 80 mL of n-heptane was poured into an 83 mm-
17 diameter pan, which was placed 600 mm below a nozzle. After a quasi-steady burning rate was
18 achieved (i.e., preburning), the nozzle was activated at a flow rate of 300 mL/min. The spray angle

1 was 50°. The average extinguishing time (τ) and its standard deviation (σ) were determined from ten
2 trials for each microemulsion.

3

4 **3. Suppression Mechanisms**

5

6 Fig. 4 presents a schematic model of the suppression mechanisms by the ferrocene-containing O/W
7 microemulsions. When O/W microemulsion droplets are sprayed onto fires, micron-sized water
8 droplets and ferrocene-containing nano-sized oil droplets readily evaporate, releasing ferrocene
9 molecules into the flames. As described above, ferrocene readily decomposes and breaks down to
10 produce active iron species, such as FeO, FeOH, Fe, and Fe(OH)₂ [34]. Several numerical and
11 experimental studies have reported that the suppression efficiency of iron compounds is sensitive to
12 the concentrations of the iron species. [10,16]. Below superequilibrium concentrations, iron-catalyzed
13 radical recombination is not effective at trapping radicals; in contrast, a very high concentration of
14 iron species acts as a trigger for lowering the suppression efficiency owing to the condensation and
15 agglomeration of the active iron species among themselves. This implies that an optimum
16 concentration of ferrocene should be added into the flames. Ferrocene-based fire-extinguishing agents
17 are promising candidates due to their low optimum ferrocene concentrations and high extinguishing
18 efficiencies.

1

2 **4. Results and Discussion**

3

4 *4.1 Emulsion Stability*

5

6 The time required for the phase separation of the O/W emulsions containing 1000 ppm ferrocene
7 and SN/OE was short (SN: <30 min, OE: <20 min). This result and the fact that the O/W emulsions
8 were opaque imply that they were macroemulsions.

9

10 Fig. 5 shows the variations of the phase separation of the O/W emulsions containing 1000-ppm
11 ferrocene and the surfactant as a function of storage time at 25 °C (Fig. 5a: surfactant = NT, Fig. 5b:
12 surfactant = TX). Note that the *PS* value is given in terms of vol%. In this figure, the more unstable
13 emulsions exhibited higher phase separation values and no phase separation was observed when *PS* =
14 0. For the NT-containing O/W emulsions with $R_{NT} \leq 3.0$ (Fig. 5a), the emulsion phases rapidly
15 separated within 180 min, whereas no phase separation was observed at $R_{NT} \geq 3.5$ for at least 25
16 months. As depicted in Fig. 5b, for O/W emulsions containing TX, phase separation occurred within
17 180 min at $R_{TX} = 2.0$ – 4.0 ; however, we confirmed that phase separation did not occur for the O/W
18 emulsion with $R_{TX} = 5.0$ for at least 25 months.

19 Fig. 6a shows a digital photograph of the O/W emulsions (surfactant = NT and $R_{NT} = 3.5$). In this

1 figure, the emulsions containing 100, 500, and 750 ppm ferrocene are in the left, center, and right Petri
2 dishes (93 mm in diameter and 15 mm in height), respectively. Fig. 6b presents the appearance of the
3 O/W emulsions (surfactant = TX and $R_{TX} = 5.0$). In this figure, the emulsions containing 100, 500,
4 and 1,000 ppm ferrocene are in the left, center, and right Petri dishes, respectively. All the emulsions
5 depicted in these figures were completely transparent for at least 25 months at room temperature; the
6 yellow coloration was due to ferrocene itself. The fact that these O/W emulsions were transparent and
7 stable over long periods indubitably indicates that they are microemulsions. Fig. 6c shows the O/W
8 emulsion containing 100 ppm ferrocene and NT ($R_{NT} = 1.0$), in which phase separation readily
9 occurred as noted above. In this case when $R_{NT} = 1.0$, the solution is undoubtedly an opaque
10 macroemulsion.

11

12 *4.2 Emulsion Droplet-Size Distribution*

13

14 In this section, the Sauter mean diameters of the stable O/W “microemulsions” containing NT and
15 TX are discussed. Hereafter, the microemulsion containing NT, x wt% oil, and y -ppm ferrocene is
16 referred to as “ME_{NT} (x, y),” and the corresponding microemulsion containing TX is referred to as
17 “ME_{TX} (x, y).”

18 Table 1 lists the Sauter mean diameters of the oil droplets (SMD_o) for the microemulsions

1 containing 2.1 wt% n-octane, 0–1,000 ppm ferrocene, and the surfactant (NT or TX). The weight ratios
2 of n-octane to the surfactants (NT and TX) were $R_{NT} = 3.5$ and $R_{TX} = 5.0$. As seen in the table, the oil-
3 droplet sizes averaged ~ 10 nm. In general, microemulsions have droplets with diameters of
4 approximately 10–50 nm [25]; the transparency of microemulsions is attributed to nano-sized droplets,
5 which are significantly smaller than the visible wavelengths of light. The observation of droplet sizes
6 of ca. 10 nm also provides evidence of the formation of microemulsion systems. For the
7 microemulsions containing NT, it is clear that there is no significant difference in the oil-droplet size
8 for different ferrocene concentration (0–1,000 ppm); the same is true for the microemulsions
9 containing TX. This result indicates that, in the ferrocene concentration range of 0–1,000 ppm, the
10 ferrocene concentration has little influence on the Sauter mean diameter of the oil droplet in the
11 microemulsion system. In addition, no significant difference in terms of the SMD_0 values was observed
12 between NT- and TX-containing microemulsions; thus, the influence of the oil-droplet size on the fire-
13 extinguishing efficiency is negligible.

14

15 4.3 Flash-Point Measurements

16

17 The Tag closed-cup tests revealed that no microemulsions tested in this study ignited below 93 °C.
18 This is because the concentration of n-octane was too low to ignite the microemulsion, thus

1 demonstrating that the microemulsions pose little ignition risk during handling and storage. Although
2 the surfactants, experimental conditions, and fuel concentrations were not identical, the results of this
3 study are consistent with the finding of Lee et al. that n-octane/water emulsions have very low flame
4 propagation velocities, even at an n-octane concentration of 80 vol% in emulsions [35].

6 *4.4 Suppression Experiments*

7
8 In this section, the pool-fire extinguishing ability of the microemulsions containing NT is
9 investigated. The reason for this investigation is that this study aimed to directly and simply evaluate
10 the influence of ferrocene on the extinguishing capability of microemulsions; for the microemulsions
11 containing TX, we observed some foaming that positively affects the suppression efficiency. Table 2
12 presents all the samples tested in extinguishing trials, including an aqueous solution of NT (hereafter
13 referred to as NT soln.), the microemulsions, and a wet chemical agent. Typical photographs of fire
14 suppression by pure water mist and ME_{NT} (2.1, 750) are shown in Fig. 7.

16 *4.4.1 Influence of oil concentration on extinguishing time*

17 As described above, the microemulsions used in this work contained a small amount of flammable
18 oil used for dissolving ferrocene. Hence, the suppression effects of ferrocene must surpass the

1 flammability of the oil in the system. In this subsection, the influence of the oil amount on the
2 suppression efficiency was investigated. The suppression trials were performed at a constant ferrocene
3 concentration of 100 ppm and n-octane concentrations ranging from 2.1 wt% to 10.5 wt%.

4 The extinguishing times for $ME_{NT}(2.1, 0)$, $ME_{NT}(2.1, 100)$, $ME_{NT}(4.2, 100)$, and $ME_{NT}(10.5,$
5 $100)$ are graphed in Fig.8. $ME_{NT}(2.1, 0)$ had an average extinguishing time of ca. 21 s. As expected,
6 the extinguishing time of $ME_{NT}(2.1, 100)$ was reduced by a factor of approximately 2.5, compared
7 with that of $ME_{NT}(2.1, 0)$ by adding 100 ppm ferrocene ($ME_{NT}(2.1, 100)$): $\tau = 7.9$ s). However, ME_{NT}
8 $(4.2, 100)$ exhibited a longer extinguishing time of approximately 9 s, and $ME_{NT}(10.5, 100)$ was
9 unable to extinguish pool fires, thereby implying that the flammability of 10.5 wt% oil surpasses the
10 suppression efficiency of 100 ppm ferrocene.

11 Interestingly, even though $ME_{NT}(10.5, 100)$ contained no less than 36.8 wt% NT, it was unable to
12 extinguish the pool fire. Thus, the use of NT as a surfactant eliminates the need to consider the
13 influence of the surfactant on the suppression efficiency.

14

15 *4.4.2 Influence of ferrocene concentration on extinguishing time*

16 As noted above, measuring the spray droplet size as well as the oil-droplet diameter in
17 microemulsions is of great importance for evaluating the fire-suppression efficiency. Table 3 gives the
18 Sauter mean diameters of the spray droplets (SMD_m) from an aqueous NT solution, $ME_{NT}(2.1, 0)$,

1 ME_{NT} (2.1, 100), and ME_{NT} (2.1, 1000). There were no significant differences in the SMD_m values
2 among these samples, which clearly indicates that the oil and ferrocene concentrations negligibly
3 affect the spray droplet size. This is probably because the concentrations of n-octane and ferrocene
4 were too low to affect the Sauter mean diameters (n-octane: 2.1 wt% and ferrocene: 0–1,000 ppm).
5 Together with the result given in subsection 4.1.1, which showed that the surfactant had little
6 suppression effect, the above finding enables us to directly investigate the influence of the ferrocene
7 concentration on the extinguishing efficiency.

8 Fig. 9 presents the average extinguishing times for the microemulsions containing 2.1 wt% n-
9 octane, NT, and 0–1000 ppm ferrocene; R_{NT} was set to 3.5. In this figure, the extinguishing times for
10 an NT soln. and a wet chemical agent (an aqueous solution of 45 wt% potassium carbonate) are also
11 shown for reference. We confirmed that pure water mist cannot extinguish the pool fire, whereas the
12 NT. soln. is able to suppress it ($\tau = 14.7$ s, $\sigma = 5.9$ s) under the same experimental conditions (i.e.,
13 flow rate, temperature, pool-fire size). The microemulsion without ferrocene (i.e., ME_{NT} (2.1, 0)) had
14 an extinguishing time of 20.6 s with a standard deviation of 5.1 s; the increase in the extinguishing
15 time relative to the NT. soln. arose from the flammability of the oil. However, the extinguishing time
16 steeply decreased at a ferrocene concentration of 100 ppm (ME_{NT} (2.1, 100): $\tau = 7.9$ s, $\sigma = 3.5$ s), i.e.,
17 the extinguishing time of ME (2.1, 100) is reduced by a factor of 2.6 compared with that of ME_{NT} (2.1,
18 0). Suppression trials also provided τ values of 5.6, 5.9, 4.5, and 6.2 s for ME_{NT} (2.1, 250), ME_{NT} (2.1,

1 500), ME_{NT} (2.1, 750), and ME_{NT} (2.1, 1,000), respectively. The wet chemical agent had an
2 extinguishing time of 8.9 s [17]. This result clearly indicated that the microemulsions exhibit a higher
3 suppression efficiency than the conventional fire suppressant.

4 A one-way analysis of variance (ANOVA) was conducted to test for differences in the
5 extinguishing times among the microemulsions: ME_{NT} (2.1, 0), ME_{NT} (2.1, 100), ME_{NT} (2.1, 250),
6 ME_{NT} (2.1, 500), ME_{NT} (2.1, 750), and ME_{NT} (2.1, 1,000). In this work, differences were considered
7 to be significant if the p -value was smaller than 0.05. The one-way ANOVA revealed significant effects
8 of the ferrocene concentration on the extinguishing time ($F = 40.80$, $p < 0.001$). *Post hoc* tests clearly
9 indicated that ME_{NT} (2.1, 0) exhibited a significantly longer extinguishing time than ME_{NT} (2.1, 100)–
10 ME_{NT} (2.1, 1000) ($p < 0.001$). Furthermore, *post hoc* tests also revealed that there were no significant
11 differences in the extinguishing times among ME_{NT} (2.1, 100)– ME_{NT} (2.1, 1,000). This suggests that
12 the ferrocene concentration required in the microemulsion system is less than ~100 ppm, which is a
13 great practical advantage in industrial processes.

14 The present work clearly demonstrated that the new O/W microemulsion-based fire suppressants
15 would be effective on class B fires; further work regarding class A fires is required. Although ferrocene
16 possesses an HMIS and NFPA rating of 2 for health (i.e., it may be harmful if inhaled or absorbed,
17 Sigma–Aldrich safety data sheet, product number F408), the new fire suppressants developed in this
18 work contain ferrocene concentrations of the order of ppm, thus indicating that health and

1 environmental risks would be low when the suppressant is used with a handheld fire extinguisher.

2

3 **5. Conclusions**

4 In this work, new oil-in-water emulsions containing ferrocene (0–1,000 ppm) and four surfactants
5 (SN, OE, TX, and NT) were prepared by homogenizing n-octane solutions of ferrocene and aqueous
6 surfactant solutions at room temperature. Four emulsion parameters were then characterized: emulsion
7 stability, emulsion droplet size, flammability, and fire-suppression capability. The main results
8 obtained from this study can be summarized as follows:

9

10 (1) Emulsion stability experiments demonstrated that phase separation rapidly occurred for the O/W
11 emulsions containing SN or OE, whereas no phase separation was observed for at least 25 months
12 for the transparent O/W emulsions containing TX or TN with $R_{TX} \geq 5.0$ or $R_{NT} \geq 3.5$, respectively.

13 For the transparent O/W emulsions, droplet-size measurements of the oil in the emulsions using
14 dynamic light scattering revealed that the oil-droplet size was ca. 10 nm, clearly indicating that
15 the thermodynamically stable emulsions are “microemulsions.”

16 (2) Droplet-size measurements also demonstrated that, in the ferrocene concentration range 0–1,000
17 ppm, no significant differences were observed in terms of the Sauter mean diameter between the
18 oil droplets in the microemulsions and their spray droplets, thus allowing a direct comparison of

1 their fire-extinguishing efficiency.

2 (3) Flash-point measurements confirmed that no microemulsions tested in this study ignited below
3 93 °C.

4 (4) Suppression trials involving pool fires clearly demonstrated that ferrocene-containing
5 microemulsions exhibit a higher suppression efficiency than a conventional wet chemical agent
6 in the 100–1000 ppm ferrocene concentration range. Furthermore, one-way ANOVA and *post hoc*
7 tests revealed that there are no significant differences in the extinguishing times among ME_{NT} (2.1,
8 100)–ME_{NT} (2.1, 1000), which means that the ferrocene concentration in the microemulsion
9 system need not be more than 100 ppm.

10

11 In conclusion, even though 2.1 wt% flammable oil (i.e., n-octane) exists in the oil-in-water
12 microemulsions, ferrocene-containing microemulsions exhibit high pool-fire extinguishing efficiency,
13 due to flame inhibition by ferrocene. The findings presented in this paper open new avenues for
14 developing novel, phosphorus-free microemulsion-based fire suppressants.

15

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16

17 **Table captions**

18 Table 1

1 The Sauter mean diameters of oil droplets (SMD_o) in the O/W microemulsions containing 2.1 wt% n-
2 octane, 0–1000 ppm ferrocene, and a surfactant: NT or TX.

3

4 Table 2

5 Samples tested in the suppression trials.

6

7 Table 3

8 The Sauter mean diameters of spray droplets (SMD_m) from an aqueous NT solution and
9 microemulsions. For the microemulsions, R_{NT} is 3.5. The aqueous NT solution contained 7.35 wt%

10 NT.

11

12

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14

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16

17 **Figure captions**

18 Figure 1

1 Trend in market prices of phosphate rock from 2000 to 2016 (adapted from [4]).

2

3 Figure 2

4 Chemical structures of (a) ferrocene and the surfactants: (b) Surfynol 465 (SN, $m+n = 20$), (c) Olfin

5 E1020 (OE, $m+n = 30$), (d) Noigen TDS-80 (NT, $R = \text{CO}(\text{CH}_2)_{16}\text{CH}_3$), and (e) Triton X-100 (TX, m

6 = 10).

7

8 Figure 3

9 Schematic of the experimental apparatus used for the suppression trials.

10

11 Figure 4

12 Schematic model of the suppression mechanism of ferrocene-containing O/W microemulsions.

13

14 Figure 5

15 Phase separation for the O/W emulsions containing 1000 ppm ferrocene and the surfactants as a

16 function of storage time: (a) surfactant = NT, and (b) surfactant = TX. The squares, circles, triangles,

17 stars, and pentagons denote $R = 2.0, 3.0, 3.5, 4.0,$ and $5.0,$ respectively.

18

1 Figure 6
2 Photographs of (a) O/W microemulsions containing 2.1 wt% n-octane, 0–750 ppm ferrocene, and NT
3 ($R_{NT} = 3.5$; left Petri dish: 100 ppm ferrocene, $ME_{NT} (2.1, 100)$; center Petri dish: 500 ppm ferrocene,
4 $ME_{NT} (2.1, 500)$; right Petri dish: 750 ppm ferrocene, $ME_{NT} (2.1, 750)$), (b) O/W microemulsions
5 containing 2.1 wt% n-octane, 0–1000 ppm ferrocene, and TX ($R_{TX} = 5.0$; left Petri dish: 100 ppm
6 ferrocene, $ME_{TX} (2.1, 100)$; center Petri dish: 500 ppm ferrocene, $ME_{TX} (2.1, 500)$; right Petri dish:
7 1000 ppm ferrocene, $ME_{TX} (2.1, 1000)$), and (c) an O/W macroemulsion containing 2.1 wt% n-octane,
8 100 ppm ferrocene, and NT ($R_{NT} = 1.0$). Note that the emulsions shown in (a) and (b) were
9 photographed 25 months after preparation, and the emulsion presented in (c) was photographed
10 immediately after preparation because of its instability.

11

12 Figure 7

13 Typical photographs of fire suppression trials: (a) pure water, after 0 s, (b) pure water, after 15 s, (c)
14 pure water, after 30 s, (d) pure water, after 45 s, (e) O/W $ME_{NT} (2.1, 750)$, after 0 s, (f) O/W ME_{NT}
15 $(2.1, 750)$, after 2.5 s, (g) O/W $ME_{NT} (2.1, 750)$, after 5.0 s, and (h) O/W $ME_{NT} (2.1, 750)$, after 5.4 s.

16

17 Figure 8

18 Influence of oil concentration on the extinguishing times of the microemulsions. Error bars indicate

1 standard deviations.

2

3 Figure 9

4 Influence of ferrocene concentration on extinguishing times (open bar: aqueous NT solution, gray bar:

5 microemulsion not containing ferrocene, yellow bars: ferrocene-containing microemulsions, and

6 striped bar: wet chemical agent containing 45 wt% potassium carbonate). Error bars indicate standard

7 deviations.