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ORIGINAL ARTICLE

Development of bio-friendly fluorine-based industrial detergents for the increase in flash point

Byung Sun Kim[1,2] · Byeong Hyeon Han[1,3] · Hyun Sik Kang[1] · Soon Wook Kwon[1] · Seung Kyu Park[2] · Kibeom Kim[4]

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Abstract

Objective Trichlorethylene, a substance of very high concern (SVHC), has been widely used as a degreasing or cleaning material for metal parts and surfaces. However, it is being replaced by detergents blended with trans-1,2-dichlorethylene (tDCE) and other compounds owing to the regulation of SVHC use in various countries. However, tDCE is difficult to use in some processes because of its low flash point. Therefore, it is necessary to develop a new bio-friendly detergent additive that can reduce the flammability of the synthesized detergents.

Methods The synthesis of heptafluoro-3-(2,2,2-trifluoroethoxy)propane (HFP), a new substance, was confirmed by nuclear magnetic resonance and Fourier transform infrared (FT-IR) spectroscopy, and the effect of detergents containing HFP was confirmed through the dyne pen, contact angle, and FT-IR.

Results With the addition of HFP, the flash point of the detergent increased, the detergent containing HFP did not exhibit metal corrosion, and the cleaning effect was maintained.

Conclusion The developed HFP is expected to contribute to the development of bio-friendly detergents because it has low biotoxicity and can be used in various industrial cleaning processes. This is because detergents containing HFP exhibit low corrosiveness and excellent cleaning effects.

Keywords Bio-friendly · Industrial detergents · Substances of very high concern

Introduction

Exposure to tens of thousands of chemicals poses a major threat to human health and the environment [1, 2]. In recent years, public awareness of the potential risks associated with the use and consumption of chemicals has increased significantly [3, 4]. Therefore, the use of substances that have detrimental effects on the human body after long periods of exposure is limited, and those substances are replaced with more bio-friendly compounds. [5, 6]

Trichloroethylene (TCE) is an organic solvent frequently used in various fields as a degreasing agent for metal parts and the cleaning of metal surfaces, and it is one of the most widely used substances of very high concern (Fig. 1a) [7–11]. Its popularity results from its high solubility, applicability to different types of material, noncombustibility, and cost effectiveness. However, TCE diffuses in a vapor state and is easily absorbed into the body through the respiratory system or skin. The absorbed TCE is delivered through the blood and acts on the central nervous system, causing various symptoms, such as headache, dizziness, vomiting, and,

✉ Seung Kyu Park
skpark@hoseo.edu

✉ Kibeom Kim
kibumsy@syu.ac.kr

1 JHC Co., Ltd, 48 Dureungyuri-Ro, Ochang-Eup, Cheongwon-Gu, Cheongju-Si, Chungcheongbuk-Do 28104, South Korea

2 Department of Chemical Engineering, Hoseo University, 20, Hoseo-ro79beon-Gil, Baebang-Eup, Asan-Si, Chungcheongnam-Do 31499, South Korea

3 Department of Safety and Health Engineering, Hoseo University, 20, Hoseo-ro79beon-Gil, Baebang-Eup, Asan-Si, Chungcheongnam-Do 31499, South Korea

4 Department of Chemistry and Life Science, Sahmyook University, 815, Hwarang-Ro, Nowon-Gu, Seoul 01795, South Korea

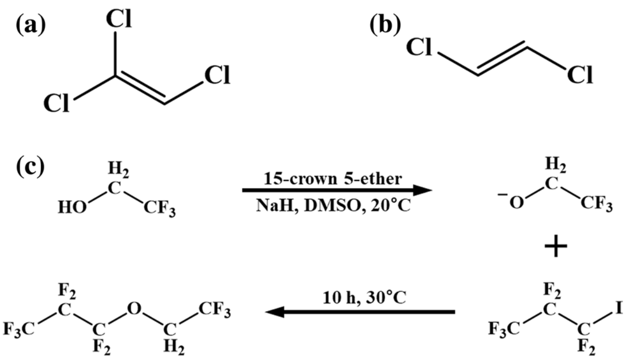


Fig. 1 Structure of **a** TCE and **b** tDCE. **c** synthetic scheme for HFP

in severe cases, loss of consciousness or death [3, 12, 13]. Furthermore, repeated exposure to TCE leads to health problems, such as liver damage, Stevens–Johnson syndrome, and cancer. Thus, the use of TCE is restricted in several countries, including European countries and the United States [4, 14–16]. However, owing to the lack of organic solvents to replace TCE, it is still used in industry to clean metals. Recently, some facilities have moved from TCE solvents to more bio-friendly trans-1,2-dichloroethylene (tDCE) (Fig. 1b). tDCE is blended with compounds used in conventional detergents such as dimethyl carbonate and dibromomethane to effectively clean industrial greases and oils from metal surfaces [17–19]. However, the use of tDCE is limited in exothermic cleaning processes, such as ultrasonic cleaning, rinsing, and vapor degreasers, because tDCE has flash point of less than 6 °C. [20] Therefore, to overcome this problem and utilize it in various processes, it is necessary to develop a new fluorine-based material that is not subject to harmful regulations and to develop an industrial detergent product that suppresses flammability while maintaining cleaning effect by blending the new material with tDCE.

In this study, a synthesis method for heptafluoro-3-(2,2,2-trifluoroethoxy)propane (HFP) with fewer than six carbon chains is presented, and its novel properties as a new additive are described. Fluorine compounds with fewer than six carbon–fluorine bonds were decomposed in a natural environment, which facilitated the synthesis of low-flammability detergents because the halogen gas generated during combustion blocks oxygen. The synthesized HFP was confirmed through nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy, and the biocompatibility was compared with that of TCE and tDCE, which are components of conventional detergents, through cell experiments using the NIH 3t3 (fibroblast cell line). In addition, the possibility of using the new compound as a detergent additive was confirmed by comparing the metal corrosion properties, flammability, and cleaning effect after blend with dimethyl carbonate, dibromomethane, and tDCE.

The various metal was immersed in the detergent which contained the HFP to observe the corrosiveness of the prepared detergent. The flammability inhibitory effect of synthetic additives was conducted by measuring the flash point of detergents with different HFP contents. Various method, which are dyne pen, contact angle and IR was conducted to confirm the cleaning effect.

Results and discussion

HFP, a fluorine-based material that is not subject to regulation, was synthesized as an additive agent to reduce the flammability without decreasing the cleaning effects of tDCE. Sodium hydride and 15-crown 5-ether were added to trifluoroethanol to convert the alcohol to enolate and to react with perfluorpropyl iodide to synthesize HFP, as confirmed by F-NMR and FT-IR (Fig. 1c). Figure 2a shows the F NMR spectrum—^{19}F-NMR (300 MHz, CDCl3): δ − 75.80 (–OCH$_2$CF$_3$), − 75.95 (–CF$_2$CF$_2$CF$_3$), − 76.10 (–OCF$_2$CF$_2$–), − 76.45 (–OCF$_2$–). The peak at δ − 75.8 was generated by the trifluoromethyl attached to the hydrocarbon. The peak at δ − 75.95 was generated by the trifluoromethyl attached to the difluoromethyl. The presence of peaks at δ − 76.10 corresponds to the difluoromethyl moiety attached between trifluoromethyl and difluoromethyl. The peak at δ − 76.45 was generated by the difluoromethyl attached to the oxygen atom. Furthermore, the HFP structure was confirmed by FT-IR spectroscopy. As shown in Fig. 2b, the characteristic absorption peak of stretching vibrations of C–O appears at 1008 cm^{-1}. In addition, the absorption peaks of the C–F group occurred at 1302–1430 cm^{-1}. These NMR and FT-IR result imply that HFP was successfully synthesized.

Repeated exposure of TCE caused various diseases, and it was regulated in European countries and the United States. To circumvent this problem, a more bio-friendly tDCE is alternating the TCE. Therefore, in order to effectively utilize the synthesized HFP, the toxicity of HFP should be confirmed. A cell experiment was conducted to compare the toxicities of TCE, tDCE, and HFP. NIH 3T3 cells, which are fibroblast cells, were incubated with TCE, tDCE, and HFP. After incubation, cell cytotoxicity was confirmed using the MTT assay. The IC50 values of TCE and tDCE were 29.81 and 137.05 mM, respectively, but the HFP IC50 values were not calculated within the experimental range (Fig. 3). These results suggest that commonly used TCE showed the highest toxicity, and tDCE showed lower toxicity than TCE. In particular, the synthesized HFP showed lower toxicity than tDCE as well as TCE, which means that the addition of HFP to existing detergents does not affect the toxicity increase of detergents. Therefore, the use of HFP with low toxicity contribute to the development of bio-friendly detergents.

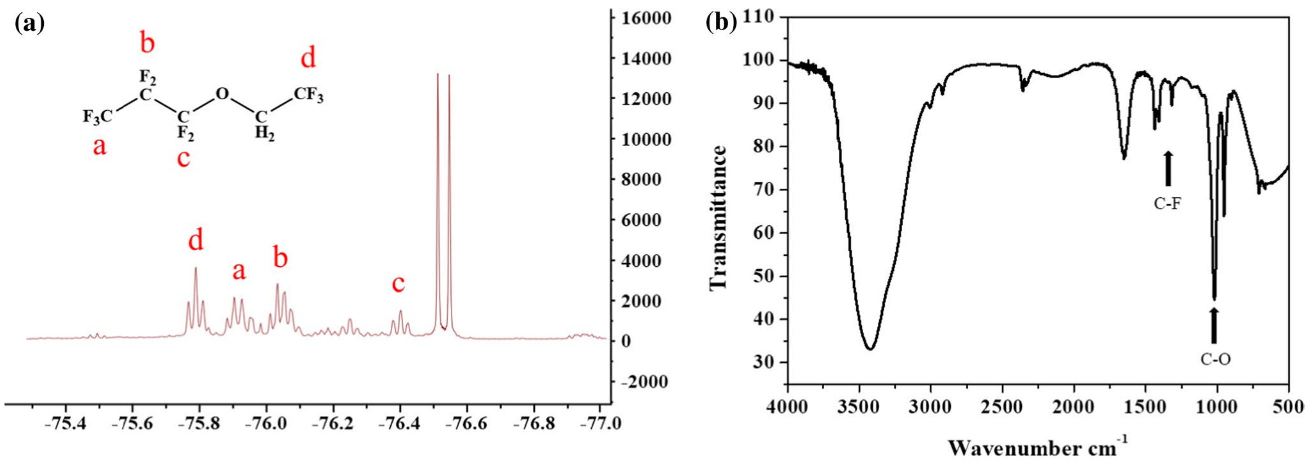


Fig. 2 **a** ^{19}F NMR and **b** FT-IR spectrum data of HFP

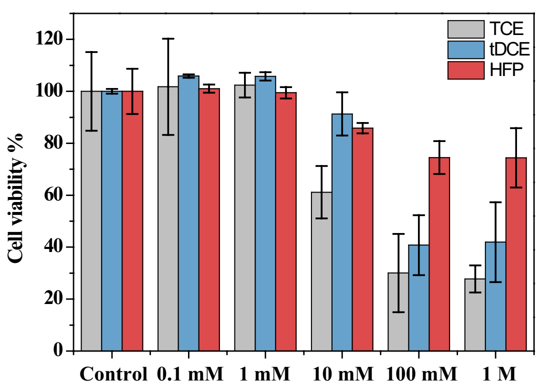


Fig. 3 Cell viability test of TCE, tDCE, and HFP

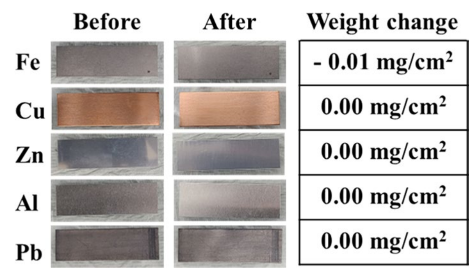


Fig. 4 Metal corrosion test of detergents containing HFP

Table 1 Changes in flash point according to HFP content

%	Control	2.5%	5%	10%
Flash point	5.5	7.0	9.5	11.0

The synthesized HFP was added to a detergent composed of dimethyl carbonate, dibromomethane, and tDCE to compare its metal corrosion ability, flammability, and cleaning effect. Because the cleaning process is mostly performed on metal machines, surfactants must have low corrosivity to prevent malfunction and the damage of cleaning machines. To check the corrosiveness of the prepared detergent, the prepared metal (iron, copper, zinc, aluminum, or lead) was immersed in the detergent, and heat was applied for 60 min, after which the surface and weight changes of the metal were examined. No significant surface and weight changes were observed for any of the metals, and a negligible weight decrease was observed only in iron (0.01 mg/cm^2) (Fig. 4). This result suggests that prepared detergent containing HFP has low corrosiveness to various metals, which shows the applicability of detergents in various processes. tDCE-based detergents have a low flash point and are limited to use in the exothermic cleaning process. An additive is added to increase the flash point of detergents. To overcome this limitation, the flammability of detergents must be suppressed through additive addition. The flash point of the detergent without HFP and the detergents containing 2.5%, 5%, and 10% HFP were measured to confirm the decrease in flammability of the detergent caused by HFP. The flash point of the detergent without HFP was 5.5 °C, but the flash point increased to 7.0 °C, 9.5 °C, and 11.0 °C in the detergent with HFP (2.5%, 5%, and 10%, respectively). Detergents containing 10% HFP had twice the flash point than detergents without HFP (Table 1). This result indicates that an increase in the HFP content decreases the flammability of the detergent by increasing its flash point.

Dyne pen is an experiment that compares the degree of contamination of surfaces by marking on a contaminated surface and an uncontaminated surface. Dyne pen shows regular marking at the high interaction between ink and substrate, whereas irregular marking at the low interaction between ink and substrate. Because antirust oil has low interaction with ink, the presence of antirust oil on the substrate was confirmed through a dyne pen. To confirm the cleaning effect of the HFP contained detergent, metal contaminated with antirust oil was cleaned with detergent and then marked with a dyne pen. The antirust oil covering the metal surface interfered with the marking of the dyne pen, resulting in irregular marking of the dyne pen on the contaminated metal; however, the dyne pen could regularly mark the metal after cleaning with detergent, regardless of whether it contained HFP (Fig. 5). This result suggests that both detergents HFP contained detergents and detergents without HFP effectively cleaned antirust oil contaminating the metal surface.

In addition, the cleaning effect was confirmed by measuring the contact angle after dropping water onto iron, copper, and aluminum surfaces. The contact angles of water on the iron, copper, and aluminum before contamination are 87.12°, 88.21°, and 86.15°, respectively. However, after antirust oil contamination, the surface hydrophobicity increased, and the contact angle of water increased to 97.63°, 97.90°, and 96.06° for iron, copper, and aluminum, respectively. As a result of washing the antirust oil on the metal surface with detergent containing HFP, the contact angles of water with iron, copper, and aluminum were 86.95°, 87.25°, and 85.70°, respectively, which are similar to the initial values (Fig. 6). This result is thought to be because the interaction between the surface and water increased as the antirust oil on the metal surface was removed. To see the difference in more detail, the cleaning effect of detergent containing HFP was confirmed by FT-IR data. Because antirust oil absorbs IR light between 2700 and 3000 cm^{-1}, after cleaning the antirust contaminated-indium tin oxide (ITO) glass with detergents containing HFP, antirust oil remaining on the ITO was confirmed by observing the change of FT-IR spectrum at the 2700–3000 cm^{-1}. The FT-IR spectrum of bare ITO glass has a wide band between 2000 and 4000 cm^{-1}, the FT-IR spectrum of antirust oil-contaminated ITO glass showed a band in the range of 2700–3000 cm^{-1} in addition to the spectrum of ITO (Fig. 7a, b). After the contaminated ITO glass was cleaned using detergents containing HFP, the FT-IR band at the 2700–3000 cm^{-1} was disappeared. As shown in Fig. 7d, FT-IR spectrum of cleaned ITO glass perfectly matches with the FT-IR spectrum of bare ITO glass. This implies that the antirust oil with an absorption band between 2700 and 3000 cm^{-1} was completely cleaned by the detergent. Dyne pen, contact angle, and FT-IR spectrum data all suggest that detergent containing HFP effectively cleans antirust oil on the substrate.

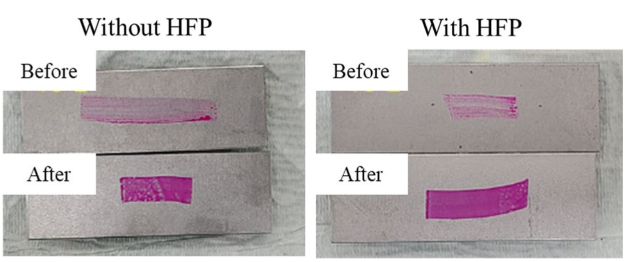
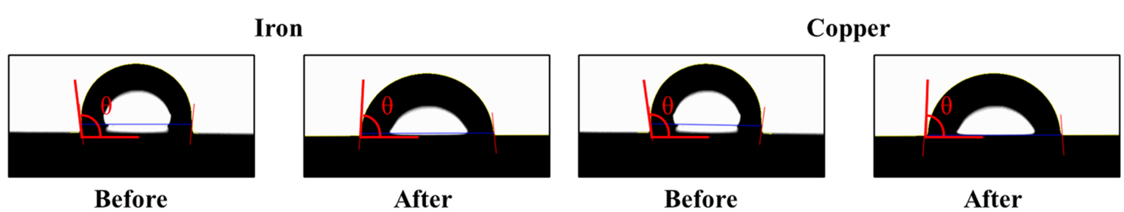


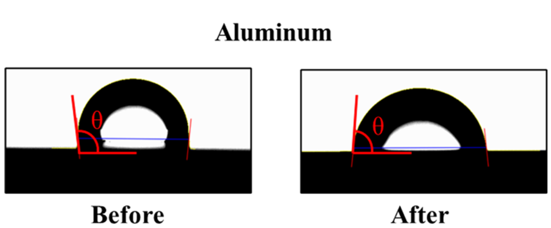
Fig. 5 Cleaning effect test using a dyne pen

Materials and methods

Materials

Dibromomethane, dimethyl carbonate, dimethyl sulfoxide (DMSO), sodium hydride, TCE, and tDCE were purchased from Sigma-Aldrich (St. Louis, MO, USA). 15-crown 5-ether, heptafluoropropyl iodide, and trifluoroethanol were purchased from TCI (Tokyo, Japan). Antirust oil was purchased from Bex-inter corporation Seoul, Korea).





Contact angle

θ	Blank	Before	After
Fe	87.12	97.63	86.95
Cu	88.21	97.90	87.25
Al	86.15	96.06	85.70

Fig. 6 Cleaning effect test using the contact angle

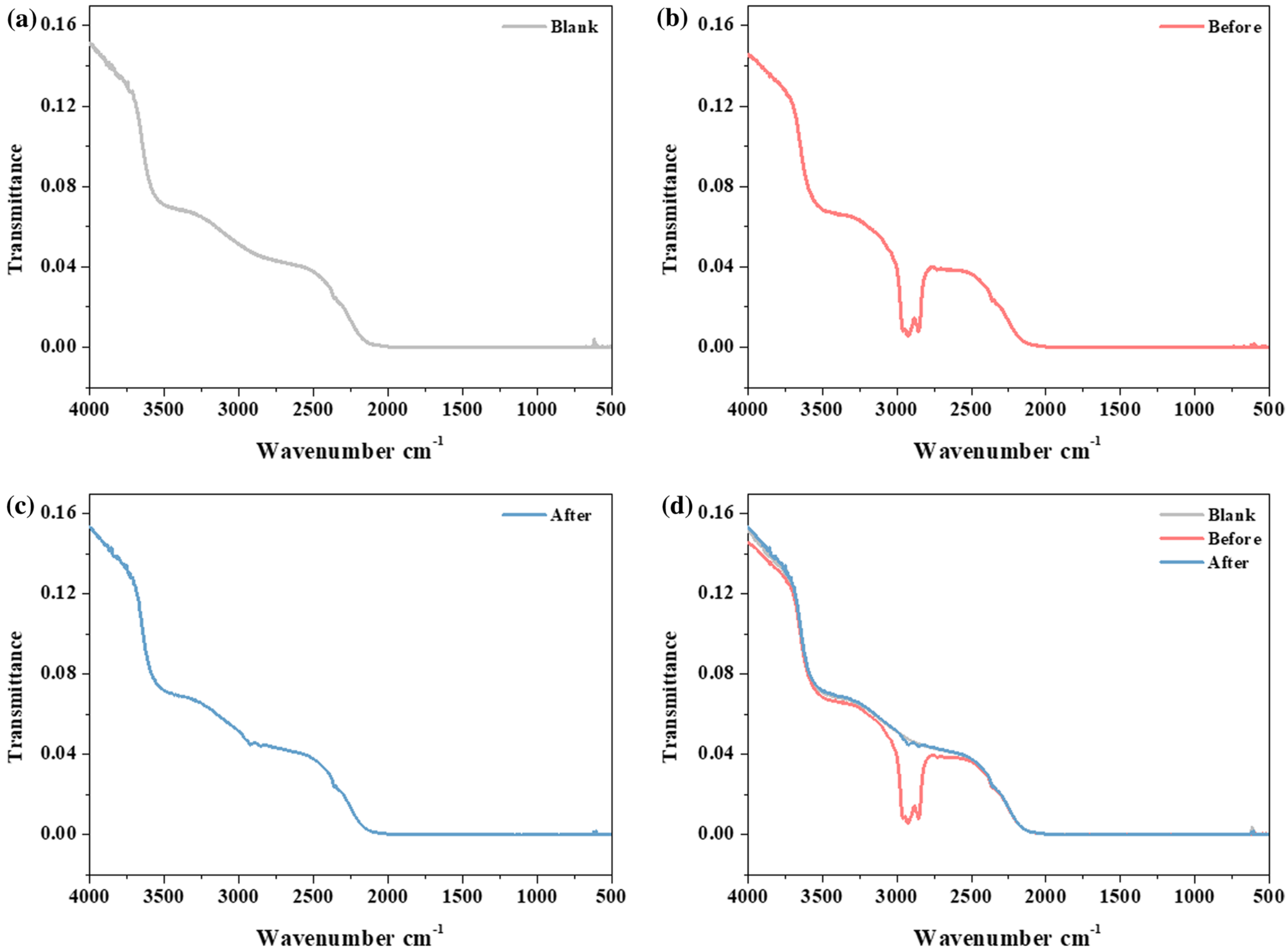


Fig. 7 **a** Bare ITO, **b** oil-contaminated ITO, **c** cleaned ITO, and **d** merged FT-IR spectrum data

Instruments

The contact angle was measured by contact angle analyzer (Gyeonggido, Korea, SEO PHOENIX300). The structure of the HFP was confirmed using NMR (Tokyo, Japan, JEOL LTD., JNM-ECZs). The flash point of detergents was measured using flash point tester (Huston, USA, Petroleum Analyzer Company LP Herzog OptiFlash Tag). The cleaning effect of the detergents was measured using FT-IR spectroscopy (Ettlingen, Germany, Bruker OpticsEquinox 55).

Synthesis of HFP

Sodium hydride (0.06 mol), 15-crown 5-ether (0.03 mol), and trifluoroethanol (TFE) were dissolved in dimethyl sulfoxide at 20 °C. Heptafluoropropyl iodide (0.03 mol) was then added. The resulting solution was heated to 30 °C in an oil bath and stirred for 10 h. The product was separated from DMSO by distillation at 90 °C. The separated product was purified by extraction with deionized water. The extraction process was performed three times to obtain pure HFP.

Toxicity analysis of TCE, tDCE, and HFP

Cell studies were performed to evaluate the toxicity of TCE, tDCE, and HFP using the NIH 3t3 (fibroblast cell) cell line. Cells with a density of 3×10^3 cells/well were cultured overnight in DMEM containing 10% FBS and 1% penicillin/streptomycin at 37 °C in a 5% CO_2 incubator. DCT, TCE, tDCE, and HFP were then added to each well at concentrations of 0.1 mM, 1 mM, 10 mM, 100 mM, and 1 M. After 24 h, the MTT assay was performed using a microplate reader at 570-nm absorption.

Preparation of detergents

To prepare the new detergents, dimethyl carbonate, dibromomethane, tDCE, and HFP were blended at 46%, 25%, 20%, and 10% (w/w), respectively. To adjust the HFP content to 10%, 5%, and 2.5% (w/w), the tDCE content was changed to 20%, 25%, and 27.5% (w/w), respectively. In addition, the tDCE content was increased to 30% in the control, and no HFP was added.

Flash point measurement

The prepared detergents having different content ratios of HFP (10%, 5%, and 2.5%) were analyzed with a flash point tester. This experiment was conducted at the Korea Testing and Research Institute (Ulsan, Korea).

Metal corrosion test

The prepared metal plate was immersed in detergent containing HFP at 50 °C for 3 h and then dried. The effect of the detergent on metal corrosion was confirmed by observing the changes in the surface condition and weight of the metal plate.

Detergent cleaning effect test using dyne pen, contact angle, and FT-IR

After the antirust oil was dropped onto the prepared metal plate, it was stored in a 90 °C oven for 1 h for the preparation of the antirust oil-contaminated metal plate or ITO glass. The contaminated metal plate or ITO glass was immersed in detergent containing HFP, irradiated by ultrasonication at 25 °C for 1 min, and dried, and the cleaning effect was confirmed using a dyne pen, the contact angle, and FT-IR.

Conclusions

As awareness of environmental pollution and human health increases, the demand for detergents with good degradability and low toxicity is increasing. However, substances that can be adjusted in various processes with excellent cleaning effects and low toxicity have not yet been developed. Recently, the use of nonregulated substances, such as tDCE, to achieve low toxicity to users by blending them with existing detergents has increased. However, tDCE has a low flash point and high flammability, making it difficult to use in various processes. Therefore, it is necessary to develop an additive that can decrease flammability while maintaining the cleaning effect of the detergent. The synthesized HFP not only showed low toxicity compared with the existing TCE and tDCE but also improved the flash point when added to an existing detergent based on tDCE. In addition, the detergent containing HFP showed a good cleaning effect, as confirmed through the dyne pen test, contact angle, and FT-IR. HFP is applied in various cleaning processes; as an additive, it should contribute to the bio-friendly development of the cleaning industry.

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Declarations

Conflict of interest Byung Sun Kim, Byeong Hyeon Han, Hyun Sik Kang, Soon Wook Kwon, Seung Kyu Park, and Kibeom Kim declares that they have no conflicts of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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