Environmental Chemistry Related to Forest Fires and Fire Extinguishers

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ABSTRACT

In recent years, large-scale forest fires and wildfires have become an increasingly major problem globally. In addition to the devastating damage inflicted by the fires, the use of harmful fire extinguishing agents has also caused serious environmental problems. Forest fires also constitute an environmental problem in terms of the generation of deleterious products, such as polycyclic aromatic hydrocarbons and dioxins, as well as the disappearance of forests. Herein, based on examples of forest fires in Japan, we describe the chemical properties of fire extinguishing agents and flame retardants that potentially cause environmental problems, as well as prospects for new technologies that are both effective and environmentally-benign.

Keywords: Forest Fire, Environmental Problem, Chemistry, Fire Extinguisher

1. INTRODUCTION

In recent years, large-scale wildfires have been occurring worldwide with increasing frequency, and 60,000 to 140,000 km² of forests are disappearing annually [1]. The damage caused by forest fires does not only constitute a dire environmental problem due to burning, but may also produce chemical secondary damage, depending on the extinguishing agent used. In such forest fires and wildfires, plants burn and then ash is produced. The damage from the fire may spread to towns and other areas, and components other than carbon in the ash, carcinogenic polycyclic aromatic hydrocarbons, and dioxins may be mixed. The ash immediately flows into rivers due to precipitation, etc., and accumulates in the surrounding soil. Such ash is likely to have a major negative impact on ecosystems [2].

In the present study, we examine three major fires that occurred in northern Kanto, Japan, in the first half of 2021. The cause of one of the fires was tobacco, the cause of the other two are currently under investigation, and these fires continued to burn for...
23, 4, and 3 days, respectively [3]. In the former case, why did the fire spread due to the mismanagement of tobacco? The temperature in the center of a lit cigarette is 700 to 800 °C, and just because a cigarette fire falls on a combustible material does not mean that it immediately produces a flame and burns. Specifically, the surroundings of the tobacco are slowly heated, the combustibles are carbonized, the temperature gradually increases, a flameless phenomenon occurs, and smoke containing flammable gas is generated. This kind of combustion is termed “smoking”, and although it continues to be in a slow state at the beginning of combustion, it is difficult to discern when it is on fire [4a]. Moreover, one of the causes of the spread of fire is flying fire, typically propagated by sparks. Sparks range from several millimeters to several tens of centimeters [3]. Flying fire causes a new fire in a remote location where the spread of fire is not expected [5]. Indeed, the fire can spread over an enormously wide area due to this jumping fire phenomenon.

When combustible substances, such as trees and wood, that form a forest start burning, the heat of reaction is generated, and the heat heats the area around the burning part to make it hotter. In addition, the state in which combustion perpetuates easily is continuous. Since a series of mechanisms continue without stopping in the special environment of a forest area and the fire does not abate, a long period of time is required to extinguish the fire, even with continuous fire extinguishing activities. As the wood is heated, the water contained in it gradually evaporates, and after reaching 100 °C, the surface turns a light brown color as the temperature rises. Then, at approximately 200 °C, the wood components, such as cellulose and lignin start pyrolysis, generate flammable gas, such as carbon monoxide and hydrogen, and nonflammable gas, such as carbon dioxide and water vapor, and 250 °C. Subsequently, when this is achieved, the rate of thermal decomposition further increases. The portion where the decomposition of the combustible material is completed also becomes ash as a combustion residue. This series of phenomena continues until the combustibles are exhausted [4c]. Furthermore, when a dry wind blows, the momentum of the fire becomes stronger [4c].

### 2. VARIOUS FIRE EXTINGUISYING AGENTS

#### 2.1 Extinguishing Agents in Aerial Spraying for Forest Fire Control

In firefighting, water has been used as the cheapest fire extinguishing agent, but various chemical fire extinguishing agents are ubiquitously employed. In large-scale forest fires, sprinkling fires are extinguished by aircraft, but a small amount of fire extinguishing agent that can efficiently extinguish the fire is required [6, 7]. The chemicals used for aerial fire extinguishing of forest fires mainly constitute two types delivery: a fire spread inhibitor that works to delay the spread of fire; and a foaming/penetrant that works to augment the fire extinguishing ability of water.

Many fire spread inhibitors contain ammonium phosphate as the main component.
One of their major disadvantages is that the fire spread inhibitor is stored as a powder, and an aqueous solution having a concentration of approximately 10 to 20% is prepared and employed at the time of use. However, since the dissolved concentration at the time of use is high, it is necessary to include many raw materials. One major advantage is that their fire extinguishing effect persists even after spraying and drying.

Fire spread inhibitors are mainly composed of synthetic surfactants, and many of them are supplied as a liquid to prepare a diluted solution of 1% or less at the time of delivery. In addition, the number of raw materials is small, and the workability is excellent. When they dry, however, they lose their fire extinguishing effect, and they need to be sprayed over a wide area [8, 9]. A fire extinguishing agent containing a gelling agent having a surfactant can be stored in a dry state, however, and becomes a gel when water is added. It is then possible to extinguish the fire [10].

The main component of the fire spread inhibitor is also used in fertilizers, and even if it is sprayed in the air during a forest fire, it is considered to produce little significant impact on the environment. However, since synthetic surfactants do not lose their surfactant action for a certain period of time even when released into the environment, it is possible that they may inhibit the respiration of gills in fish and cause their suffocation. The gel-like fire extinguisher consists of at least one type of fatty acid metal salt component having 10 to 18 carbon atoms and one type of metal sequestering agent component, and is not easily decomposed by microorganisms. As a consequence, it may have a negative impact on the environment [8].

2.2 Firefighting Foam

Foam fire extinguishing agents extinguish fires through a cooling and choking effect. They are used for oil fires, such as fires involving oil tanks and underground/indoor parking lots, and fires that may be particularly challenging to extinguish with water alone. In addition, they are stored in an undiluted state, diluted with seawater or water to the specified concentration when utilized, and released as bubbles. They are mainly classified into the following five categories.

Protein foam fire extinguishing agent [11]

In this type of agent, fire extinguishing speed is slow due to poor foam fluidity. However, since the combustion oil surface is covered at a stable speed and the foam layer remains on the oil surface for a long period of time even after the fire is extinguished, the relapse prevention effect is excellent. Therefore, it is suitable for large-scale oil tank fires, in which there is a risk of relapse due to the influence of the red-hot tank wall.

Fluorine protein foam fire extinguishing agent [11]

The fluoroprotein foam fire extinguisher is a protein foam fire extinguisher with a small amount (several %) of fluorine-based surfactant added. Fluoroprotein foam has more than twice the non-combustibility performance as protein foam because of the
flammability of gasoline pollution with protein foam. Normally, when the fixed foam fire extinguishing equipment of an oil tank does not work sufficiently due to an earthquake, etc., foam is emitted directly from the outside to the combustion surface using a high-altitude water discharger, but the fluoroprotein foam is contaminated by oil. Since there are few bubbles and the fluidity is good, the fire extinguishing effect is markedly superior to protein bubbles.

Fluorine-based surfactant foam fire extinguishing agent [11]

This agent has the ability to significantly reduce the surface tension of organic solvents, such as water and petroleum, and rapidly spread the molecular film of the fluorine-based surfactant on the liquid surface. In addition, the molecular film of the fluorine-based surfactant on the oil surface is oil. It has the ability to form a molecular film because it significantly suppresses the evaporation of oil. Due to the fluorocarbon group, it is chemically stable, withstands long-term storage, and possesses excellent chemical resistance.

Synthetic surfactant foam fire extinguishing agent [12]

This agent has excellent low-, medium- and high-foaming properties, is effective for initial fire extinguishing and spilled oil fires, and quickly flows and deploys the fire oil level to extinguish the fire rapidly. It also possesses excellent adhesion and wettability to wood and other solid combustibles.

Foam fire extinguishing agent for water-soluble liquid [13]

This agent has excellent alcohol resistance and is ideal for extinguishing water-soluble liquids. It is also effective in extinguishing petroleum fires because it possesses remarkable properties as a fluorine protein foam fire extinguishing agent, such as fluidity, fire resistance, and oil pollution resistance.

2.3 Fluorinated Foam Firefighting Agents

Some firefighting foam products contain ingredients that are internationally recognized to cause environmental problems. Here, the component perfluorooctanesulfonic acid (abbreviated as PFSO) of the organic fluorine foam fire extinguisher will be described (Figure 1). It has water and oil repellency, low surface tension, non-adhesiveness and low friction [14], persistence, bioaccumulative property, exhibits toxicity and long-distance migration, and has persistent organic pollutants. It has been designated as a harmful substance and has been internationally regulated with the aim of its elimination [15]. In 2009, in the Stockholm Convention on Persistent Organic Pollutants, "PFOS or its salt" Annex B (manufacturing and use), Import / export restrictions. In Japan, it was designated as a Class 1 Specified Chemical Substance under the Chemical Substances Examination Regulation Law (Chemical Substances Control Law) in 2010, and manufacturing, importing, and use, except for some uses, were totally banned in 2018.
In Japan, the use of PFOS-containing foam fire extinguishing agents was originally prohibited because it does not fall under the Essential Use Regulations of the Chemical Substances Control Law (if there are no exceptionally recognized alternative substances and there is no health effect) [17]. However, since a considerable quantity has already been deployed nationwide and it is difficult to replace it with a short-term alternative product due to its usage, it will continue to be used if it is handled in accordance with technical standards concerning labeling and storage.

In fact, a major accident occurred at a military base involving PFOS. Approximately 227,100 liters of PFOS foam fire extinguishing agent leaked, of which 143,830 L, more than 60%, spilled into the private sector [18]. The soil around the leaking hangar was removed 14 days later, but the removed soil was submitted one month after the accident [19].

Since April 2010, the manufacture and use of PFOS-containing products has been prohibited [15]. In May 2020, PFOS was added to the items requiring monitoring regarding the protection of human health in public water bodies and groundwater. Furthermore, as a guideline value, which is a provisional target, the total value of PFOS was set to 0.00005 mg / L or less (50 ng / L or less) [20]. The Ministry of the Environment continues to promote measures, such as the substitution of foam fire extinguishing agents containing PFOS, in cooperation with related ministries and organizations.

Furthermore, fluorine-based perfluorooctanoic acid (abbreviated as PFOA) (Figure 2), which exhibits similar properties to PFOS, has been widely used as a raw material for Teflon processing of frying pans and water-repellent processing of food wrapping paper [18]. Indeed, its persistent nature in the environment and accumulation in the living body are regarded as major problems.
An aqueous film is observed on the surface of heptane when the fluorine-based foam is sprayed [21]. At the same flow rate and expansion rate, fluorinated foam spreads faster than fluorinated foam. Fluorine-free foam solutions have high surface tension and high viscosity, which slows the spread of bubbles. Therefore, by increasing the foam flow rate and decreasing the expansion coefficient, the fluorine-free foam can spread rapidly on the heptane surface [22].

The difference in stability between fluorine-free foam and the fluorine-containing foam is consistent with the observation of the interaction with the oil film. Oil droplets become unstable by spreading on a fluorine-free film, but tend to be rapidly discharged from the fluorine-containing film in the form of an oil lens, which slightly affects the stability of the film [23].

### 2.4 Synthetic Surfactants and Flame Retardants

In this section, chemical features of typical synthetic surfactants for flame retardants will be briefly introduced.

**Anionic surfactant (Figure 3)**

Hydrophilic groups are carboxylate (-COONa), sulfate ester salt (-OSO$_3$Na), etc., and they do not easily lose their role as surfactants by reacting with sodium contained in hard water. Sulfate salts are acidic and easily decomposed, and those having an ester bond, such as -COOCH$_2$-, in the molecule are easily decomposed by alkali or acid [24a, b].

**Cationic surfactant (Figure 4)**

Hydrophilic groups are amine salts and quaternary ammonium salts. Amine salts have low water solubility and are stable only in acids. Quaternary ammonium salts are highly water-soluble and are acidic to alkaline, and most of them are stable. Cationic surfactants have opposite characteristics to anionic surfactants, and thus mixing them will result in precipitation [24c].
Amphoteric surfactant (Figure 5)

Amphoteric surfactants have anions and cations in the hydrophilic group, some of which are carboxylates and sulfates. Most amphoteric surfactant agents are carboxylic acid salts, those having an amine salt type cation moiety are amino acid amphoteric surfactant agents, and those having a quaternary ammonium salt type cation moiety are betaine amphoteric surfactant agents. Amino acid-type amphoteric surfactants behave like anionic surfactants when alkaline, become less hydrophilic and precipitate at isoelectric points, and behave like cationic surfactants when acidic. In contrast, betaine amphoteric surfactants are highly water-soluble at any pH and can be used at any pH [24d].

Nonionic surfactant (Figure 6)

Nonionic surfactant has a hydroxyl group (−OH) or an ether bond (−O−) that does not dissociate ions in water as a hydrophilic group. The polyethylene glycol type is made by adding ethylene oxide as a hydrophilic group to a hydrophobic group raw material, which has both an ether bond and a hydroxyl group as a hydrophilic group. In addition, many polyhydric alcohols have a hydrophobic group, such as a higher fatty acid. The polyethylene glycol type has high water solubility and is used for detergents and the like. Many polyhydric alcohol types are insoluble in water and are used as fabric softeners [24e].

Figure 6 Example of a cationic surfactant

Figure 5 Example of an amphoteric surfactant

Figure 6 Example of a nonionic surfactant
3. FLAME RETARDANTS

Fire retardants, which are not used in forest fires but are ubiquitous, are effective when incorporated into materials. They are similar to fire extinguishing agents, however, in that the harmfulness of the chemicals that remain after use (burning) presents a threat. According to the Building Standards Law, the temperature of the object itself becomes high, but it ignites slowly. In fact, it does not burn, does not cause harmful damage (deformation, welding, cracks, etc.) in terms of fire protection, and does not produce smoke that is harmful in terms of evacuation. After ensuring that no gas is generated, flame retardants are classified, depending on the heating time, as a "non-combustible material" (kept for 20 min after the start of heating) [25], "quasi-non-combustible material" (kept for 10 min after the start of heating) [26], and "flame-retardant material" (kept for 5 min after the start of heating) [27]. Then, control of heat transfer, i.e., control of temperature rises due to heating of the material, control of thermal insulation of the solid surface. Pyrolysis rate control reduces the generation of flammable gas or decomposes the entire amount of flammable gas before it reaches the combustion temperature. Control of pyrolytic substances will reduce the amount of flammable gas in the generated gas, and makes it hard to burn. Control of gas phase reaction is released in the gas phase, in which a substance that suppresses the combustion reaction. A compound having these four combustions suppressing effects is called a "flame retardant".

Current issues regarding flame-retardant materials include the development of environmentally-friendly (non-harmful and smoke-resistant) materials, high-performance flame-retardant materials, materials with excellent recyclability, and materials with outstanding molding processability. Recent studies have reported that the more easily are the materials pyrolyzed, the more the combustion is inhibited [28]. Among flame retardants, halogen-based, antimony, and phosphorus-based elements require attention from the perspective of safety and environmental harm. Halogen-based brominated flame retardants include polybrominated biphenyls, polybrominated diphenyl ethers, hexabromocyclododecane, tetrabromobisphenol A, etc. Chlorinated flame retardants include chlorinated paraffin. These halogens and antimony trioxide, when combined with $\text{Sb}_2\text{O}_3$, exhibit high flame retardant performance due to a synergistic effect [29a]. Phosphorus, which is a non-halogen type due to environmental problems, is attracting attention, as well as red phosphorus type and phosphoric acid. Typical examples are triphenyl phosphate, which is used as a flame retardant for business equipment and personal computers [29b] (Figure 7).
Figure 7 Examples of flame retardants. (a) Polybrominatedbiphenyl, (b) Polybrominatedbiphenylether, (c) 1,2,5,6,9,10-Hexabromocyclododecane, (d) 2,2’,6,6’-Tetrabromobisphenol, (e) 2,3,4,5,6,8-Hexachlorodecane, (f) Red phosphorus, (g) Triphenyl phosphate
4. NEW TECHNOLOGIES FOR FOREST FIRES

4.1 Chemical Sensors for Forest Fire Prevention

Other wildfire countermeasures exist that utilize chemical knowledge. For instance, sensors using an ionic liquid (a liquid in a salt in which cations and anions are bound is melted) has been developed. Conventional methods, such as observation by artificial satellites, monitoring by unmanned aerial vehicles, and observation by watchtowers have presented the problem that alarms initiate only after the fire becomes uncontrollable. In addition, wireless monitoring systems that comprise sensor networks in forests have been developed, but they also have certain major challenges, such as being composed of inorganic semiconductors that are expensive, inflexible, and harmful to the environment. Therefore, a self-powered paper chip using two types of ionic liquids was proposed. In this approach, when there is a temperature gradient, one ionic liquid has a higher potential on the hot electrode and a lower potential on the cold electrode; the case is the opposite with the other type of ionic liquid. When the two are connected in series, the voltage signal rises sharply when a large temperature difference, such as a fire, occurs and serves as an alarm. Indeed, it is an epoch-making sensor that is both inexpensive and environmentally-friendly [30].

4.2 New Strategy to Extinguish Fires

Conventional firefighting methods for forest fires include spraying water with chemicals from the air, as described in section 2-1, and extinguishing fires from the ground if a hose is available. However, a major concern exists about the environmental impact of chemicals sprayed in the air. Therefore, we propose a new method of extinguishing fires from the air using a gas-based fire extinguishing system.

In certain countries other than Japan, large aircraft and helicopters are used for aerial firefighting. Gas-based fire extinguishing systems are installed on these large aircraft. Among the gas fire extinguishing systems, carbon dioxide fire extinguishing systems reduce the oxygen concentration in the combustible mixture formed by the mixing of fuel and air, making the combustion reaction inactive. In addition, the heat capacity of carbon dioxide removes heat from the flame, which reduces the flame concentration and makes the combustion reaction inactive, thereby extinguishing the fire [4c]. The use of large aircraft loaded with gas-based firefighting equipment with these extinguishing effects for firefighting activities is expected to have a significant effect on forest fires over a wide geographical area.

5. CONCLUSION

Worldwide, forest fires burn organic matter and large amounts of related deleterious substances that can negatively affect the environment [31]. In the event of a forest fire, it is evident that a fire extinguishing agent should be utilized that does not harm
the environment as much as possible. Since foam fire extinguishing agents, which are synthetic surfactants, generate highly toxic gases, such as SO2, depending on the components, environmentally-friendly soap-based foam fire extinguishing agents have been developed. Indeed, they have been utilized not only as fire extinguishers, but also as flame retardants. Halogen-based materials have become an international problem, however, and the development of alternative materials is a critical goal of future research. Among halogens, fluorine used as a fire extinguishing agent is particularly hazardous, and chlorine contained in flame retardants can generate dioxins; thus, special care must be taken when these materials are used. In many cases, when metal-containing fire extinguishing foams [32] and flame retardants [33] are developed, performance is prioritized and environmental load is not seriously considered. Therefore, new technologies are urgently needed that simultaneously extinguish fires effectively and are environmentally-benign.

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