HOT AEROSOL FIRE EXTINGUISHING AGENTS AND THE ASSOCIATED TECHNOLOGIES: A REVIEW

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Abstract - Since the phase out of Halon extinguishers in the 1980s, hot aerosol fire suppression technology has gained much attention. Unlike traditional inert gas, foam, water mist and Halon fire suppression agents, hot aerosol fire extinguishing agents do not need to be driven out by pressurized gases and can extinguish class A, B, C, D and K fires at 30 to 200 g/m^3. Generally, hot aerosol fire extinguishing technology has developed from a generation I oil tank suppression system to a generation III strontium salt based S-type system. S-type hot aerosol fire extinguishing technology greatly solves the corrosion problem of electrical devices and electronics compared to potassium salt based generation I & II hot aerosol fire extinguishing technology. As substitutes for Halon agents, the ODP and GWP values of hot fire extinguishing aerosols are nearly zero, but those fine aerosol particles can cause adverse health effects once inhaled by human. As for configurations of hot aerosol fire extinguishing devices, fixed or portable cylindrical canisters are the most common among generation II & III hot aerosol fire extinguishers across the world, while generation I hot aerosol fire suppression systems are integrated with the oil tank as a whole. Some countries like the U.S., Australia, Russia and China, etc. have already developed standards for manufacturing and quality control of hot aerosol fire extinguishing agents and norms for hot aerosol fire extinguishing system design under different fire protection scenarios. Coolants in hot aerosol fire suppression systems, which are responsible for reducing hot aerosol temperature to avoid secondary fire risk are reviewed for the first time. Cooling effects are generally achieved through vaporization and endothermic chemical decomposition of coolants. Finally, this review discussed areas applying generation I, II or III hot aerosol fire suppression technologies. The generation III hot aerosol fire extinguishing system is most applicable, especially in areas involving delicate electrical and electronic equipments. Nonetheless, developing a much cleaner, non-corrosive and highly efficient hot aerosol fire suppression system is still needed.
Keywords: Aerosol forming agent; K-type; S-type; Aerosol forming agent cooling.

INTRODUCTION

Hot aerosol fire extinguishing technology was introduced and developed since 1960s, based on pyrotechnics. Because of the problem of ozone depletion caused by using Halon extinguishing agents which contain bromofluoroalkanes (Andrzej & Tsang, 1997), many countries joined the Montreal Protocol. This Protocol announced protective actions for the ozone layer in 1987 and promoted the phase out movement to phase out Halon extinguishants.

Compared to Halon extinguishants, other traditional extinguishants like foam, inert gas and dry powders are usually not as efficient as Halons. Those

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traditional extinguishants are also often stored in pressurized containers.

Extinguishing technology based on dry powders or particles dispersed in a solution is called cold aerosol technology. These dry and fine powders can be alkaline or alkaline earth metal carbonates, phosphates, etc. Particles dispersed in solution can be sodium, potassium or magnesium chlorides, lithium iodide, potassium acetate, sodium hydroxide, potassium ferrocyanide (Korobeinichev *et al.*, 2012), and PCCs (phosphorus containing compounds) (Jayaweera *et al.*, 2005), etc. Table 1 shows the comparison of hot aerosol fire suppression technology with other common fire extinguishing technologies.

Table 1: Comparison of suppression mechanisms of common extinguishing agents with hot aerosol technology.

Name of extinguishing agents	Suppressive mechanism
CO_2, IG-541 (N_2, CO_2 and Ar), N_2 (Richardson and Bennett, 2008)	Suffocation, dilution
Water	Cooling
Foam	Dilution, cooling
FM200 (Heptafluoropropane),1301 (Carbon monobromide trifluoride),1211 (Bromochlorodifluoromethane), fluoro methane (Chen and Yang, 2003)	Chemical inhibition
Cold aerosol	Cooling, dilution, chemical inhibition
Hot aerosol	Cooling, dilution, chemical inhibition

For hot aerosol technology, the main ingredients in the fire extinguishing aerosol forming agent are alkaline or alkaline earth metal nitrates, which act as oxidants in hot aerosol generating process, and different kinds of reductants. Classifications of hot aerosol suppression products can be seen in Figure 1.

Hot aerosol fire extinguishing agents have good efficiency in fire extinguishing and they do not need to be stored in a pressurized container since they do not need to be driven out by pressurized inert gases. A block of hot aerosol fire extinguishing agent sits in a canister with openings in the cap, and a fuse attached to the canister ignites the aerosol forming agent to generate hot aerosol, which can be driven out automatically. Hot aerosol forming agents have low ODP (Ozone Depletion Potential) and GWP (Global Warming Potential) value (Kwon & Kim, 2013). So research and development of such new fire

suppression technology have been given much attention, especially in developed countries.
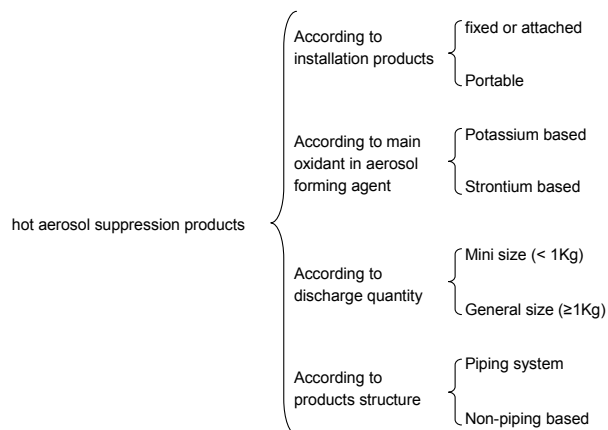

Figure 1: Classifications of hot aerosol fire suppression products.

Fire Extinguishing Mechanism of Hot Aerosol Agents

Different from traditional or cold aerosol extinguishing agents, in hot aerosol extinguishing systems, hot aerosol colloids with diameters from 10^{-9} to 10^{-7} meters are generated through redox (reducing-oxidizing reaction) of a hot aerosol forming agent. Those colloids have diameters much smaller than 4×10^{-6} m at which Brownian motion starts to occur (Fu *et al.*, 2001) and hence it gives the hot aerosol particles a high diffusive ability and a long suspension time in the fire zone to fight fire. Basically, the mechanism of hot aerosol extinguishing agents to extinguish fire is both physical and chemical.

Physical Fire Extinguishing Processes

Because aerosol particles have high surface to volume ratios, when those particles enter the fire zone, they attract fire supporting radicals such as hydrogen and hydroxyl radicals onto their surfaces by multiple layer physical adsorption, which is the premise for chemical adsorption to reduce particle surface energy and stop the burning chain reaction (Yang, 2009). Also, Agafonov *et al.*, (2004) found that gases generated by redox, like nitrogen, water vapor and carbon dioxide, can choke the fire by diluting surrounding oxygen and reduce the fire zone temperature (see Figure 2). Physical extinguishing processes contribute less than chemical fire extinguishing processes unless when the fire is near extinction (Larson, 2003).
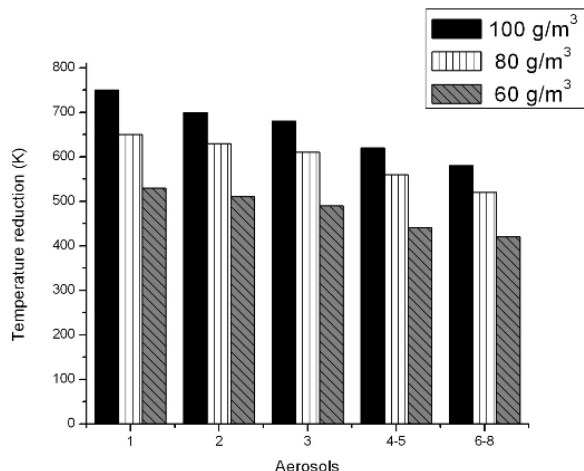
Figure 2: Temperature reductions by some aerosols on flame temperature of hydrogen-air mixture; 1: 100% KOH, 2: 50% KOH + 50% K_2CO_3, 3: 100% K_2CO_3, 4: 100% K_2O, 5: 50% K_2CO_3 + 20% N_2 + 30% CO_2, 6: 40% CO_2 + 60% N_2, 7: 100% KCl, 8: 50% KCl + 20% CO_2 + 30% N_2.

Chemical Fire Extinguishing Processes

Combustion of the oxidant with the reductant generates microparticles such as alkaline or alkaline earth oxides, hydroxides or chlorides, which can re-combine with the fire supporting radicals like hydroxyl and hydrogen radicals, etc. in the fire zone (Agafonov *et al.*, 2004; Williams & Fleming, 1999). Figure 3 shows how sodium hydroxide particles reduce fire supporting radical concentration.
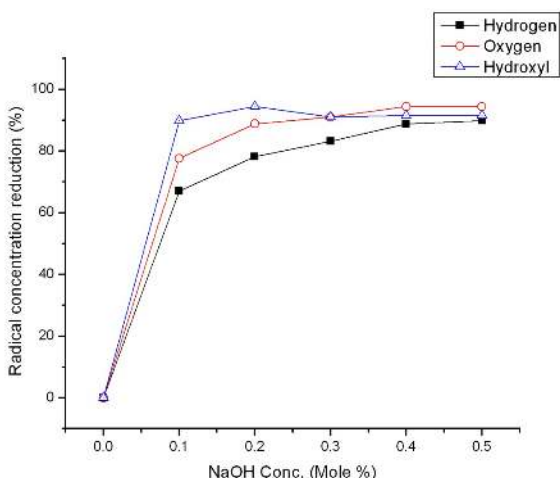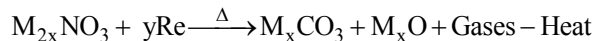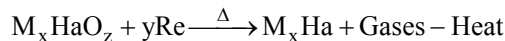

Figure 3: Sodium hydroxide concentrations vs. radical concentration reduction in methane-air mixture.

Redox product species are dependent on the anion group in the oxidant and, if the anion group is NO_3^-, then the following reaction happens:

$$M_{2x}NO_3 + yRe \xrightarrow{\Delta} M_xCO_3 + M_xO + Gases - Heat$$

If the anion group is HaO_z^- (Ha can be Cl, Br or I), then the redox becames:

$$M_xHaO_z + yRe \xrightarrow{\Delta} M_xHa + Gases - Heat$$

where M can be Na, K, Mg, Ca, Sr or Al and Re refers to reductants like sugers (glucose, sucrose, alpha-lactose, etc.) or derivatives of amides (dicyana-mide, dicyandiamide), guanidines (nitroguanidine) or cellulose (nitrocellulose). Also, reductants can be pure carbon powders or charcoal, or even reactive metal powders like aluminum and magnesium powders. Magnesium or ammonium oxalate can also be auxil-iary reductants.
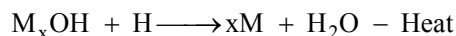
The gases are primarily CO_2, N_2, and H_2O vapor and with trace quantity of ammonia, NOx and CO if the anion group is nitrate in the oxidant. Gases can contain halogen acid if the anion group is HaO_z^-. CO_2, H_2O vapor, ammonia, NOx or even trace quantities of hydrogen cyanide can exist if the reductants are cyanoguanidines, dicyandiamide or nitroguanidine (Zhang & Tan *et al.*, 1997; Block, 1953). Reductants like metal powders will be oxidized into oxides and become the solid phase in the aerosol.

Next a decomposition reaction starts in the fire zone after redox of the oxidant whose anion group is NO_3^- decomposition reaction temperature depends on particle size and the element property, e.g., sodium carbonate decomposes at temperature above 1397 °C (Wanigarathne *et al.*, 2000).

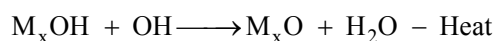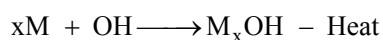$$M_xCO_3 \longrightarrow M_xO + CO_2 + Heat$$

$$M_xO + H_2O \longrightarrow M_xOH - Heat$$
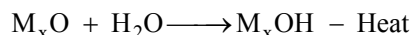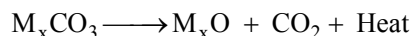
Then a fire supporting radical recombination process starts.

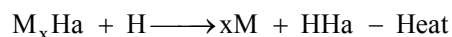Depletion of hydrogen (Birchall, 1970; Williams & Fleming, 1999):

$$M_xOH + H \longrightarrow xM + H_2O - Heat$$

Depletion of hydroxyl:

$$xM + OH \longrightarrow M_xOH - Heat$$

$$M_xOH + OH \longrightarrow M_xO + H_2O - Heat$$

Depletion of oxygen:

$$\mathbf{x}M + O \longrightarrow M_xO - Heat$$
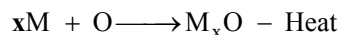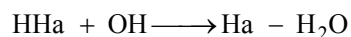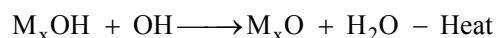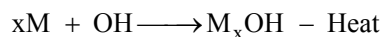
Those recombining reactions can be either heterogeneous or homogeneous because volatilization of small particles (< 5 μm) in a flame is possible. When M is the element potassium, a third party acting like a catalyst is involved in the recombination reaction (Birchall, 1970).

For the anion group HaO_z^-, the fire supporting radical recombination processes are almost same. (Birchall, 1970):
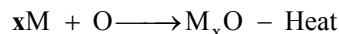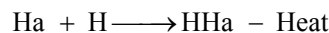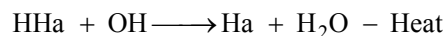
Depletion of hydrogen:

$$M_xHa + H \longrightarrow xM + HHa - Heat$$

Depletion of hydroxyl:

$$xM + OH \longrightarrow M_xOH - Heat$$

$$M_xOH + OH \longrightarrow M_xO + H_2O - Heat$$

$$HHa + OH \longrightarrow Ha - H_2O$$

Depletion of oxygen:

$$\mathbf{x}M + O \longrightarrow M_xO - Heat$$
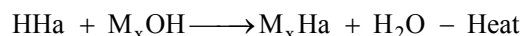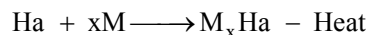
And for an oxidant with the anion group HaO_z^-, Ha radicals also participate in hydrogen and hydroxyl radical recombination processes (Sheison *et al.*, 1989):

$$HHa + OH \longrightarrow Ha + H_2O - Heat$$

$$Ha + H \longrightarrow HHa - Heat$$

When the radical recombination chain reaction terminates, halogen radicals are converted into halides with the least harm to the environment:

$$Ha + xM \longrightarrow M_xHa - Heat$$

$$HHa + M_xOH \longrightarrow M_xHa + H_2O - Heat$$

From the above reactions, the hot aerosol particles produce crucial alkaline or alkaline earth metal oxides and hydroxides through the aerosol forming agent combustion to recombine with fire supporting radicals continuously. The whole process continues until most fire supporting radicals are recombined and thus the fire is extinguished (Yang & Fu, 2000).

Since the cation and anion groups in the oxidants can be different, the fire extinguishing efficiency varies in different aerosol forming agents. Basically, the fire supporting radical binding affinity of different metal element compounds with the same anion group follow the sequence: K> Na > Sr > Ca> Mg> Al. Salts composed of different anions and the same metal cation have fire extinguishing efficiencies following the sequence: oxides> cyanides> iodides> bromides> chlorides> sulphates> phosphates (Guo & Yue, 2008).

Sulphates and phosphates are used mainly in cold aerosol and dry powder technology, and cyanides can be used as an additive in the hot aerosol forming agent to enhance fire extinguishing efficiency. However, potassium hexacyanoferrate (II), which generates potassium cyanide when it decomposes thermally (Kunrath *et al.*, 1978), is rarely used in hot aerosol fire suppression technology even though its fire extinguishing efficiency is high (Korobeinichev *et al.*, 2010).

HAZARDS CAUSED BY HOT AEROSOL EXTINGUISHANTS

Since hot aerosol particles have sizes between 10^{-9} to 10^{-7} m, so they are called PM 2.5 particulates whose aerodynamic diameters (dp) are no larger than 2.5 μm. Akeredolu pointed out that fine particles ($dp < 2.5$ μm) can deposit on the bronchi walls in the bronchial tree (Akeredolu, 1996), causing chronic respiratory diseases and acute respiratory diseases (Jimoda, 2012). Figure 4 shows the penetration of different size particulates in the human lung.
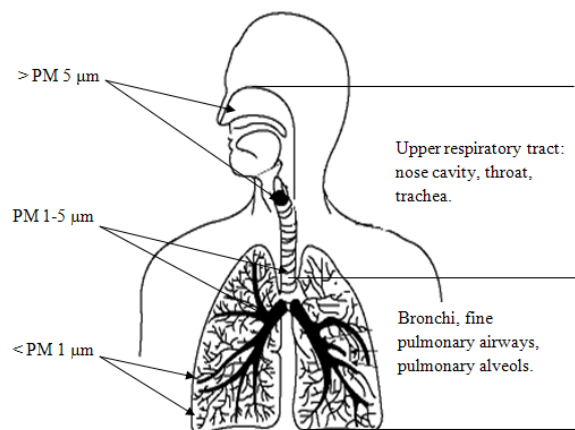

Figure 4: Penetration of particulates in human lung.

Moreover, in the gas phase of the hot aerosol, there can be NO_x, CO, CO_2 and hydrocarbons (Zhu *et al.*, 2013). Especially NO_x and CO can cause susceptibility to respiratory pathogens, reduction in the ability of the circulatory system to transport O_2, impairment of performance on tasks requiring vigilance and aggravation of cardiovascular diseases (Stern *et al.*, 1984), so strict regulations have been made in countries like the U.S., Russia, Australia and China to limit the maximum concentration of hazardous gases released by hot aerosol forming agent. Another problem caused by hot aerosol is the reduction in visibility in the fire zone since both fine particulates and gases in the hot aerosol can absorb and scatter light. Ying *et al.* (2004) reported a visual index, deciview (dV) as:

$$dV = 10 \times \ln\left(\frac{b_{ext}}{0.01 km^{-1}}\right) \qquad (1)$$

where 0.01 km^{-1} is the approximate extinction coefficient due to Rayleigh scattering in a pristine atmosphere and b_{ext} is the extinction coefficient that controls the change in the appearance of objects with distance. b_{ext} varies with the wavelength. The deciview scale is near zero for a near pristine atmosphere and increases as visibility impairment increases. Also, Ying *et al.* (2004) estimated the aerosol extinction coefficient $b_{a,ext}$ and the aerosol scattering coefficient $b_{a,scat}$ for the dimensionless scattering and extinction coefficients for the homogeneous and core-and-shell configuration as:

$$b_{a,ext} = \sum_{i=1}^{n}\sum_{j=1}^{m} \pi r_{i,j}^2 N_{i,j} Q_{e,i,j} \qquad (2)$$

$$b_{a,scat} = \sum_{i=1}^{n}\sum_{j=1}^{m} \pi r_{i,j}^2 N_{i,j} Q_{s,i,j} \qquad (3)$$

where i refers to the emission source for primary particles, j refers to size, n is the number of primary particle source categories, m is the number of particles of different sizes. N and r are the number concentration and radius of the particles, respectively. Q_s and Q_e are the dimensionless scattering and extinction coefficients, respectively (Jimoda, 2012).

Besides adverse effects on human health and impairment to environment visibility, large numbers of corrosive particles such as oxides, hydroxides and carbonates of alkaline metals together with some acidic NO_x and CO_2 gases present in the hot aerosol can damage delicate electronics and electrical equipment or treasured archives and antiques with the existence of water droplets (Zhu & Wang *et al.*,

2013), but this problem can be largely solved by substituting alkaline metals with alkaline earth metals like magnesium and strontium since their oxides, hydroxides and carbonates are insoluble. Meanwhile, high temperature aerosol produced by redox process is inevitable and hot aerosol sometimes can reach 1200 K or above at the canister nozzle (Zhu *et al.*, 2013), so hot aerosol may bring potential risks of a secondary fire. Coolants must be installed in the canister together with hot aerosol forming agent. Also, a hot aerosol shockwave happens due to release of large quantities of hot gases to the fire zone from a narrow canister space. This blast may damage the infrastructure in a room, but can also be helpful for sweeping off the fire. In countries which have standards for hot aerosol fire suppression unit installation, infrastructure damage caused by a hot aerosol blast has not been reported.

Finally, ALT (Atmospheric Lifetime), ODP and GWP values of hot aerosol forming agents are negligible (Kwon & Kim, 2013).

INGREDIENTS OF HOT AEROSOL EXTINGUISHING AGENTS

In chosing the major components for the oxidants and reductants in hot aerosol forming agents, deliquescence and hydration degree of the oxidants and reductants matter first. In addition, in the choice of reductants, the quantity and species of gases generated by the reductant after redox also matter. Additives are also important in manufacturing, storage and fire extinguishing performance of hot aerosol forming agents. For example, stearates are anti-deliquescence additives, and ammonium nitrate can be added as a minor oxidant and a redox booster, etc. Binders like epoxy, melamine, polysaccharide, phenol aldehyde or rubbers, etc. shape the hot aerosol forming agent into a firm and hard solid.

Choice of Oxidants in Hot Aerosol Forming Agents

As mentioned above, a good oxidant should not be deliquescent and contain no or few hydrates. After redox, the aerosol particle sizes, which are important for fire extinguishing, depend on the oxidant species.

Unfortunately, many oxidants like nitrates and halogenic acid salts are deliquescent and most of them contain hydrates, which make them hard to be ignited. However, less deliquescent or anhydrous oxidants can still be found.

For nitrates, Group IA element salts are all anhydrous and, for Group IIA elements, anhydrous nitrates of Be, Mg, Ca, Sr and Ba can be prepared.

However, $Be(NO_3)_2$ and $Ba(NO_3)_2$ are very toxic, so nitrates of Mg, Ca and Sr are left for consideration. The stability sequence for anhydrous nitrates of Mg, Ca and Sr is $Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2$ and the deliquescence tendency sequence is $Mg(NO_3)_2 > Ca(NO_3)_2 > Sr(NO_3)_2$; as a result, strontium nitrate is superior. As for Group IIIA elements, anhydrous aluminum nitrate is very unstable, and its non-anhydrous form is nonahydrated. Nitrates of the rest of the Group IIIA elements are either toxic or highly hydrated, so they are not ideal oxidants. The nitrate of a Group IVA element is $Pb(NO_3)_2$ and it is toxic. The nitrate of Group VA element is $Bi(NO_3)_3$, which is a pentahydrate, not ideal for combustion.

Most nitrates of transition metal elements are hydrated and toxic and their anhydrous nitrates are very unstable and deliquescent, so they are not suitable to be major oxidants. But some nitrates of transition elements like zinc and copper nitrate can be additives in hot aerosol forming agents to enhance the fire extinguishing efficiency (Zhou, 2013; Ji & Wei, 2013).

Back to Group IA elements, for fire extinguishing efficiency (See Figure 5) the sequence is Cs> Rb> K> Na> Li (Agafonov *et al.*, 2004; Williams & Fleming, 1999), and KNO_3 is a common chemical which only becomes hygroscopic at 95% relative humidity (Schönherr, 2002), so it is the best oxidant for hot aerosol forming agents, and still being widely used in hot aerosol fire extinguishing technology.
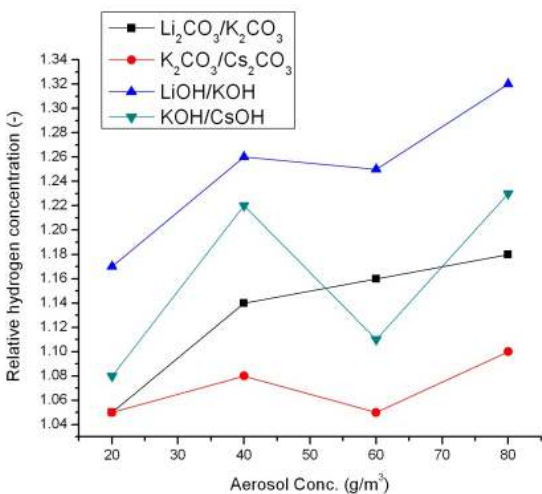

Figure 5: Comparison of alkaline metal aerosol influence on hydrogen concentration in a flame of a mixture of hydrogen and oxygen.

The halogenic acid salts, perchlorates, perbromates, periodates or chlorates, bromates and iodates of Group IA elements are all anhydrous but deliquescent and highly reactive. Aerosols of M_xHa are less efficient in fire extinguishing than M_xO (Birchall, 1970), so halogenic acid salts are less popular than nitrates as

oxidants in hot aerosol forming agents, but still some hot aerosol forming agents contain perchlorates as auxiliary or minor oxidants. Most halogenic acid salts of Group IIA, IIIA or transition metals are either highly hydrated or hygroscopic, and they are relatively expensive, so they are seldom used in hot aerosol fire extinguishing technology except for being used as auxiliary additives. Common oxidants used are listed in Table 2.

Choice of Reductants in Hot Aerosol Forming Agent

Hot aerosol fire extinguishing technology is derived from pyrotechnics. Fuels used in pyrotechnics like metals, carbohydrates or carbons are also used as reductants in hot aerosol forming agents. A good reductant in hot aerosol forming agents should be little or non-toxic, reactive and cheap, and it should produce incombustible gases as much as possible, because incombustible gases produced by reductants are important for carrying the aerosol particles and also help fire killing. Such reductants include carbohydrates like lactose, sucrose and derivatives of cellulose, or charcoal and carbon black. Derivatives of guanidines such as dicyanamide, nitroguanidine are also good reductants, which can produce large quantities of nitrogen when combusted. Nitrogen gas is clean and good for fire extinguishing (Petronella & Leenders, 2003), so derivatives of guanidine are often chosen as reductants in hot aerosol forming agents, but hydrogen cyanide gas can be formed during decomposition of cyanoguanidine (Zhang *et al.*, 1997).

Synthetic reductants like derivatives of tetrazoles, which can produce large quantities of nitrogen gas, can be considered as well. Especially 5-amino tetrazole and guanidinium azotetrazolate can be used since they are relatively stable if cautions are taken (Wang *et al.*, 2010). However, derivatives of tetrazoles are still seldom used as reductants in hot aerosol forming agents due to strict safety issues.

Metal powders can be used as reductants, too. Sometimes binders or polymers like polytetrafluoroethylene, dibutyl-phthalate, or dioctyl sebacate, together with thermoplastic formaldehyde and phenol polycondensate, can also be reductants (Denisyuk *et al.*, 2003).

Redox processes of hot aerosol forming agents are highly exothermic and raise the risk of secondary fire. By changing reductants, a relatively low combustion heat between 59.8-143.5 J/g aerosol forming agent (as compared to 205.7 J/g aerosol forming agent for the others) is achieved by using cyanuric acid, barbituric acid or hydroxyacetic acid salts of Group IA or IIA elements as reductants (Denisyuk *et al.*, 2003). Common reductants used are listed in Table 3.

Table 2: Oxidants in hot aerosol forming agent.

Products on the market (oxidant %)	Nitrates			Halogenic acid salts		
	Group IA	Group IIA	Others	Group IA	Group IIA	Others
Soviet Union in 1960s (Guo & Yue, 2008) (35%-50%)	Potassium, sodium nitrate		Ammonium nitrate	Potassium perchlorate		
Russian (Guo & Yue, 2008) (61.2%+4.8%)	Major potassium nitrate		Minor potassium ferricyanide			
Canada (Pak *et al.*, 1998) (40-70%)	Potassium nitrate					
US (Kozyrev *et al.*, 1997) (67-72%)	Potassium nitrate					
Europe (Denisyuk *et al.*, 2003) (77.5-88.8%)	Nitrate of sodium or potassium			Potassium or sodium perchlorate		
China (Fu *et al.*, 2003)	Potassium nitrate					
China (Guo & Hu, 2011) (40-55%+5-15%)	Minor potassium nitrate	Major magnesium nitrate				
China (Guo & Hu, 2011) (40-70%)		Magnesium nitrate	Aluminum nitrate			
China (Hu, 2011)	Potassium nitrate	Strontium nitrate				
US (Posson & Clark, 2012)				Halogenic acid salts of Group IA, IIA or IIIA metals		
US (Guo & Zhang, 2012) (20-35%+30-48%)	Minor Potassium nitrate	Major Strontium nitrate				

Table 3: Reductants in hot aerosol forming agent.

Products on the market (Reductant %)	Carbohydrates	Derivatives of guanidine	Carbon based	Metal or alloy powders	Others
Soviet Union in 1960s (Guo & Yue, 2008) (5%-40%)		Dicyanamide and nitroguanidine			Urea
Russian (Guo & Yue, 2008) (8.4%+0.5%)			Major charcoal		Minor diphenylamine
Canada (Pak *et al.*, 1998) (5-15%)			Carbon		
US (Kozyrev *et al.*, 1997) (16-25%)		Dicyanadiamide			
Europe (Denisyuk *et al.*, 2003) (3-11%)					Polytetrafluoroethylene and dibutyl-phthalate or dioctyl sebacate
China (Fu *et al.*, 2003)	Sucrose				
China (Guo & Hu, 2011)		Nitroguanidine			
China (Guo & Hu, 2011) (40-70%)					Hexamethylenetetramine
China (Hu, 2011)	Sucrose			Magnesium and aluminum powder	
US (Posson & Clark, 2012)					Group IA or IIA salts of cyanuric acid, barbituric acid or hydroxyacetic acid
US (Guo & Zhang, 2012) (20-35%+30-48%)		Nitroguanidine			Diazoaminotetrazole or its salts

Choice of Binders and Additives in Hot Aerosol Forming Agents

Usually, binders can be cellulose derivatives, cellulose ether, a gum, a gel or polyvinyl compounds. Epoxy and phenol aldehyde are two of the most common binders in hot aerosol forming agents; others can be nitrocellulose, hydroxyl-terminated polybutadiene, fluoroplastics, polyethylene, melamine and iditol, etc.

The functions of additives include the stabilization of redox process and enhancing the storage life of hot aerosol forming agents. Additives like carbonates of Group IA and IIA elements or magnesium oxide can slow down and smooth the redox rate, and oxides of transition elements like Fe, Cu, Ni, Mn and Cr can be catalysts for reducing carbon and nitrogen mono oxides in the aerosol gas phase (Zhang *et al.*, 2013). For storage, stearates of Group IA and IIA elements can keep the hot aerosol forming agent block dry and prevent it from growing mold.

TYPES AND CHARACTERISTICS OF HOT AEROSOL EXTINGUISHING AGENTS AND DEVICES

Through 40 years of development, hot aerosol extinguishing technology has reached the third generation, which is S-type or G3 hot aerosol extinguishing agent in which the major oxidant is strontium or magnesium salts. Historically, the first generation of hot aerosol fire extinguishing technology is called G1 fire extinguishing technology, which was invented in Tianjin, China, in the 1960s (Liu *et al.*, 2005). The second generation or G2 hot aerosol fire extinguishing technology, whose major oxidant is potassium salts, is called K-type hot aerosol extinguishing technology.

Differences and Characteristics of G1, G2 & G3 Aerosol Extinguishing Agents

The extinguishant of G1 fire extinguishing technology contains mostly potassium nitrate with a mass ratio of more than 50%, similar to K-type hot aerosol extinguishing agents.

Different from second and third generation of hot aerosol fire extinguishing technology, the first generation of hot aerosol fire extinguishing technology aims at extinguishing in-tank liquid fires such as oil, alcohol and ketone flames, etc., and the aerosol particles are not fully generated in the extinguisher canister. About 85% of the aerosol generated by G1 fire extinguishing agent are steam and inert gases com-

posed of N_2 and CO_2. Generally, this technology is deemed as the prototype of today's hot aerosol fire extinguishing technology. The G2 and G3 hot aerosol forming agents are compressed or bound into a cylindrical block during manufacturing. During the redox process, aerosols are fully generated in the canister, and then be pushed out by gases generated in the canister.

Compared to traditional Halon extinguishing agents, G2 or K-type extinguishing agents have a 4-5-fold higher fire extinguishing efficiency (Guo & Yue, 2008). Generally, the lowest concentration for G2 (K-type) hot aerosol forming agents required to extinguish a 10 cm diameter heptane pan ranges from 30-200 g/m^3 (Guo & Yue, 2008). G3 (S-type) requires at least 100 g/m^3, so K-type hot aerosol extinguishing agents have higher fire extinguishing efficiencies compared to the S-type. This is because Group IA elements have a higher reactivity with fire supporting radicals compared to Group IIA elements and oxides of Group IA elements have lower evaporation and dissociation temperatures, which make them become aerosols more easily and more readily bind fire supporting radicals compared to oxides of Group IIA elements.

Granularity affects the fire extinguishing efficiency of K and S-type aerosol forming agents greatly and it governs aerosol particle diffusion, aggregation and settlement. When fire extinguishing particles like potassium carbonates and oxides have diameters less than 10 μm, they will evaporate in the flame and then the homogeneous fire inhibition process begins (Baratov *et al.*, 1988); such fire extinguishing efficiency is very high. Oxides and carbonates of magnesium and strontium (generated from S-type) have smaller diameters, higher densities and evaporation temperatures (see Figure 6).
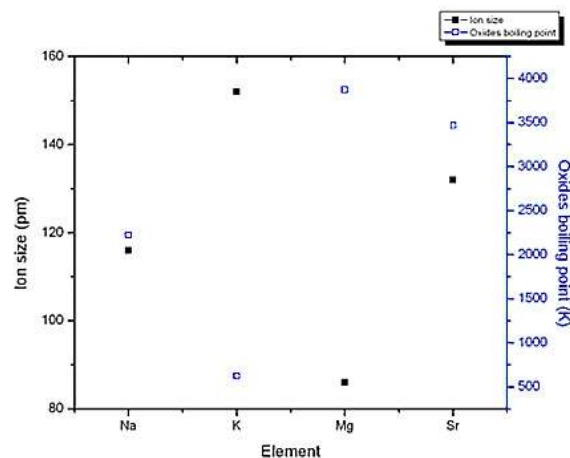

Figure 6: Ion size (filled square) and oxide boiling point (hollow square) of K-type (Na, K) and S-type (Mg, Sr) elements.

Higher evaporation temperatures of S-type aerosol particles restrict their participation in homogeneous fire inhibition process and reduce their fire extinguishing efficiency.

Moreover, according to the well-known fractal aggregation formula (see Equation (4)) (Meakin, 1983; Jullien & Botet, 1987), the smaller the diameter d_p, the higher the number of particles that aggregate, so S-type aerosol particles aggregate faster than K-type aerosols.

$$n = k_f \left(\frac{2R_g}{d_p} \right)^{D_f} \tag{4}$$

where n is the number of primary particles in an aggregate, d_p the diameter of primary particles, R_g the radius of gyration of an aggregate, D_f the fractal dimension, and k_f the fractal prefactor.

S-type aerosol aggregates with larger volume and heavier mass settle faster and thus suspend for less time in a fire zone to kill the fire according to Stokes' law:

$$v = \frac{2}{9} gr^2 \left(\frac{\rho - \rho_0}{\eta} \right) \tag{5}$$

where v is the terminal velocity of spherical particles, r the radius of particles, ρ the density of particles, ρ_0 the density of the disperse medium, g the gravitational acceleration and η the dynamic viscosity of the disperse medium. From Einstein's diffusion coefficient equation (Equation (6)), S-type aerosol particles consequently have lower diffusion coefficients than K-type particles. A low diffusion coefficient means that particles cannot spread faster in a confined room to kill the fire in a short time.

$$D = \left(\frac{RT}{6N_A \pi \eta r} \right) \tag{6}$$

where D is the diffusion coefficient, R the ideal gas constant, T the temperature, N_A the Avogadro number, η the dynamic viscosity of the disperse medium and r the radius of the particles.

After combustion, the gas to solid mass ratio in K or S-type aerosols ranges from 1:4 to 1: 1.14 and depends on the aerosol forming agents. In K-type aerosol, the main components in the solid phase are bicarbonates and carbonates of relevant Group IA elements, and in S-type, they are oxides, carbonates and hydroxides of Group IIA elements (Fu et al., 2003). S-type agents precipitates have higher electrical resistivity, which can reach 10^{12} Ω, since the precipitates are not deliquescent or soluble, while the surface resistivity of K-type precipitates normally does not exceed 10^5 Ω (Liu & Dong, 2004). From industrial standards GA 499.1-2004 and GA 499.1-2010, the resistivity of a PVC plate surface covered by aerosol precipitates of the S-type should exceed at least 20 MΩ after 30 min at 35 °C and 95% humidity.

G1 Fire Extinguishing Devices

G1 hot aerosol fire extinguishing devices can be classified into in-tank or out-tank types. For both in-tank and out-tank configurations, the sprinkler head can be either upward or downward. For diesel, crude oil, heavy oils and petroleum, the in-tank configuration is adopted (Duan et al., 2007), and for alcohols and ketones, the out-tank configuration is used. See Figure 7 and 8.

G1 hot aerosol fire extinguishing technology is convenient in terms of installation and cheap in cost, but the aerosol forming agent storage stability depends on tank sealing. Advanced types developed from G1 became second and third generation (G2 & G3) aerosol fire extinguishing technologies, which have a wide range of applications besides oil tank fire extinguishing.

G2 & G3 Hot Aerosol Fire Extinguishing Devices

Basically, G2 and G3 fire extinguishing technologies have fixed/attached and portable canister structures. Fixed/attached types (see Figure 9) usually have regular cylinderal canisters of different sizes and the configuration of such canisters can be seen in Figure 10. Portable types include hand-held and grenade configurations. Fixed/attached types are designed for fire extinguishing in a large space like a warehouse, data room, etc. The hand-held type is portable for extinguishing small scale fires close to an operator. The grenade type can enable an operator to throw an aerosol grenade into the fire source from a far distance to extinguish fires and reduces the risks of injury and death of the operator.

Portable or hand-held hot aerosol fire suppression devices have the configuration shown in Figure 11. In order to ensure safe holding, an insulating layer is necessary for preventing heat transfer to the outer surface of the canister. The coolant in the canister near to the nozzle can also reduce the risk of being burnt by hot aerosol.

Usually, the aerosol discharge time of hand-held devices is longer than 15 s and fixed/attached devices have a discharge time depending on the device dimensions. In hand-held devices, the discharge time can be elongated by mixing burning retardants with aerosol forming agents so that the operator has enough time to aim at the fire source before all aerosols are discharged.
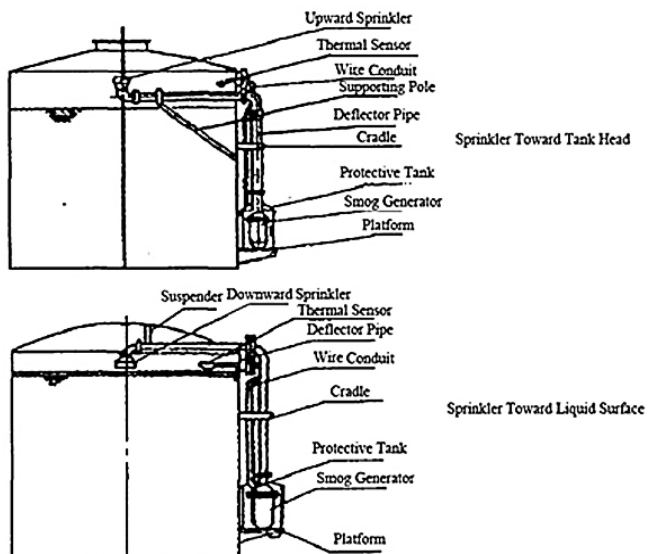
Figure 7: Out tank G1 extinguishing device. (Reproduced with permission from Duan *et al*., 2007).
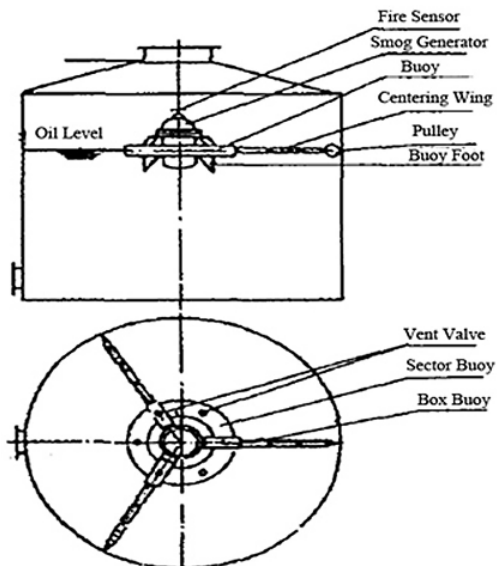
Figure 8: In tank G1 extinguishing device. (Reproduced with permission from Duan *et al*., 2007).
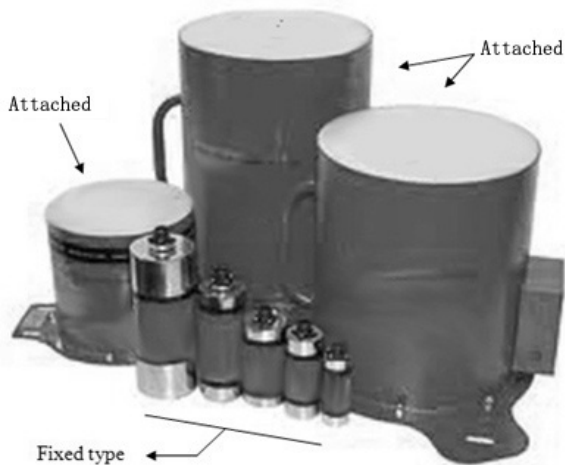
Figure 9: Fixed/attached hot aerosol fire extinguishing devices. (Reproduced with permission from Brochure Pyrogen, 2010).
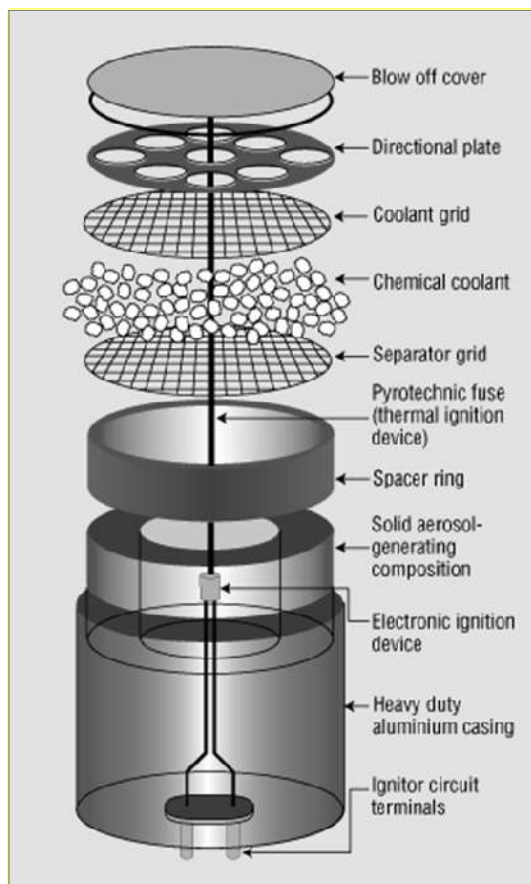
Figure 10: General configuration of hot aerosol canister. (Reproduced with permission from Brochure Pyrogen, 2010).

1 - safety pole
2 - button
3 - thermal insulating layer
4 - enclosure of cartridge
5 - chemical agent
6 - enclosure of cooling layer
7 - cooling material
8 - jet nozzle
9 - tapered jet orifice
10 - enclosure of apparatus
11 - combustion chamber
12 - groove
13 - installing hole
14 - rear fender
15 - piezoelectric ceramic
16 - U-shaped holder
17 - rear cap
18 - safety ring
19 - spongy cushion
20 - fixing hole
21 - tray
22 - retaining ring
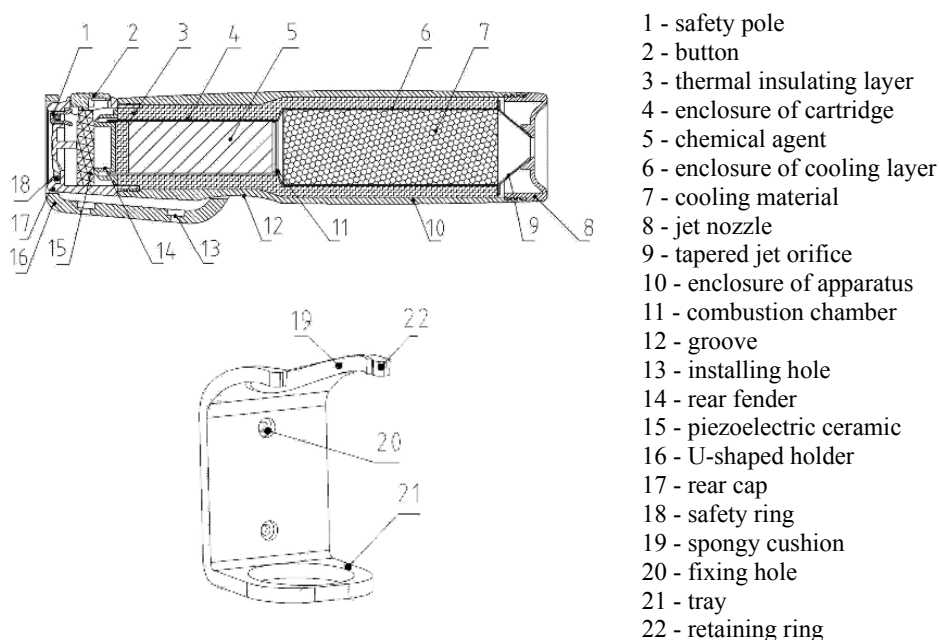
Figure 11: Hand-held hot aerosol device and mounting bracket for storage.
(http://www.google.com/patents/EP2441495A1?cl=en).

For hot aerosol fire extinguishing grenades, a pull ring attached to a pin holds the striker, which hits at a delay tube cartridge; this cartridge provides 6 to 10 s for the operator to throw the grenade into fire source before the ignition of the aerosol forming agents. See Figure 12.

Table 4 compares the differences in G1, G2 and G3 hot aerosol extinguishing technology.
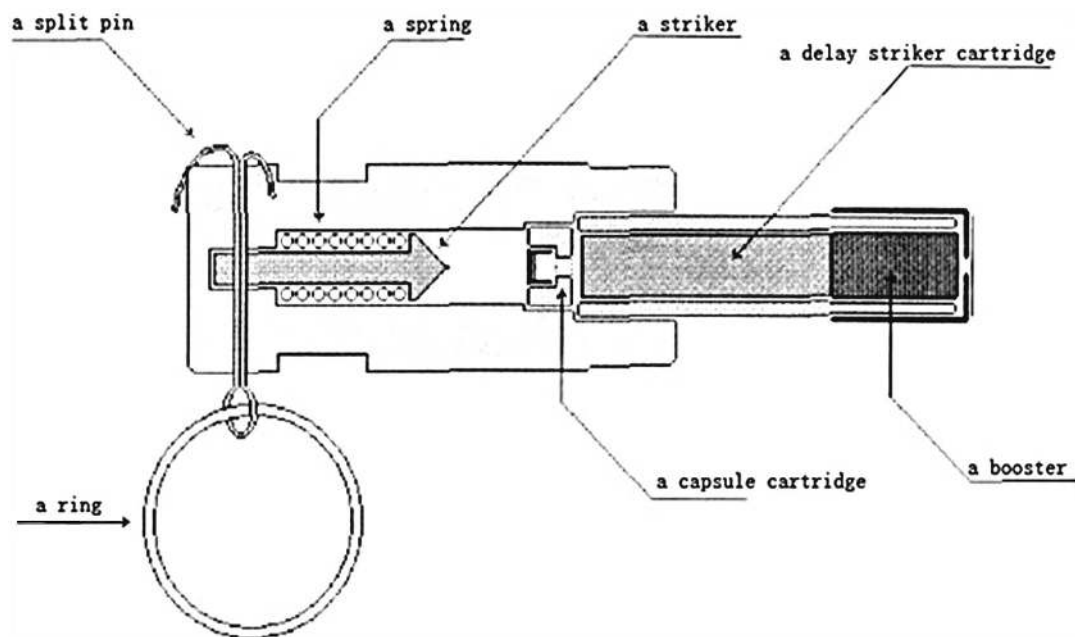
Figure 12: Aerosol grenade configuration (reproduced with permission from Berezovsky and Joukov, 1999).

Table 4: Differences of G1, G2 and G3 hot aerosol extinguishing technology.

	G1 smoke fire extinguishing technology	G2 aerosol fire extinguishing technology	G3 aerosol fire extinguishing technology
Major oxidant	Potassium Nitrate	Potassium Nitrate	Strontium/ Magnesium Nitrate
Aerosol forming method	Partially generated in canister	Fully generated in canister	Fully generated in canister
Device types	In tank or out tank	Fixed, holding, wall- mounted and grenade type	Fixed, holding, wall- mounted and grenade type
Fire aimed to be extinguished	Class B	Class A, B, C, E & K*	Class A, B, C, E & K
Application fields	Flammable liquid storage tank	Oil storage, turbine, engine compartment, warehouse, machinery space, etc. (Back & Boosinger, *et al*., 2009; Scheuermann & Modigell *et al*, 1999)	Data room, communication base, electric power room, space launching control room, etc. (Shi, 2000)

*Class A- Fires in ordinary combustible materials, such as wood, cloth, paper, rubber, and many plastics; Class B- Fires in flammable liquids, combustible liquids, petroleum greases, tars, oils, oil-based paints, solvents, lacquers, alcohols, and flammable gases; Class C- Fires that involve energized electrical equipment; Class D- Fires in combustible metals, such as magnesium, titanium, zirconium, sodium, lithium, and potassium and Class K- Fires in cooking appliances that involve combustible cooking media (vegetable or animal oils and fats).

SPECIFICATIONS AND TECHNICAL TERMS OF G1, G2 & G3 HOT AEROSOL FORMING AGENTS

The technical parameters of G1 hot aerosol fire extinguishing agents are different according to in-tank or out-tank type. See Table 5.

Technical terms for G2 and G3 hot aerosol forming agents are classified into pre-extinguishing and post-extinguishing ones to control the hot aerosol forming agents' performances. See Table 6.

Most pre-fire extinguishing terms are the same for both G2 and G3 hot aerosol forming agents, but different requirements for G2 and G3 can be found in post-fire extinguishing terms, such as effective aerosol concentration for fire extinguishing, precipitate insulation level, residues quantity, etc. G3 hot aerosol forming agents are required to be applicable in places with sensitive electrical and electronics, different from where G2 hot aerosol forming agents are commonly employed. Also, the technical terms of G1 hot aerosol forming agents are different from G2 and G3, due to their specific application in oil tank fire extinguishing. Hence, the technical terms strictly regulate quality control of hot aerosol forming agent manufacturing according to their application fields.

Table 5: G1 fire extinguishing agent technical parameters. (Reproduced with permision from Duan *et al*., 2007).

Product series		Item				
		Ignition temperature (°C)	Discharge time (s)**	Emission stroke (m)**	Fire extinguishing time (s)	Validity of agent (years)
Out-tank	ZWW5	180	<13	>4	<40	4
	ZWW10	180	<30	>7	<40	4
	ZWW12	180	<40	>8	N/A	4
In-tank	ZW12A	110	<35	>7	68~120	4*
	ZW16A	110	<40	>9	N/A	4*
Product series	ZWW5	ZWW10		ZWW12	ZW12A	ZW16A
Oil tank diameter protected (m)	≤5	≤10		≤12	≤12	≤16

*Valid under 60 °C, ** Data in CECS 169-2004

Table 6: Technical terms for G2 & G3 hot aerosol forming agents*.

Pre-fire extinguishing terms		Post-fire extinguishing terms	
Terms	**Specifications**	**Terms**	**Specifications**
Operational Environment requirements:	-20~+55 °C, Relative humidity: <95%	Fire extinguishing time:	Class A fire < 60 s Class B fire < 30 s
Agent appearance:	Smooth surface, uniform color	Effective aerosol concentration:	Concentration passes the fire extinguishing test
Discharging time:	≥1 kg, <120 s <1 kg, < 40 s	Precipitates insulation level:	> 20 MΩ for S-type, > 10 MΩ for K-type under test condition
Aerosol forming agent component content:	Less than ± 2% deviation	Aerosol Toxicity:	No lab rat death after exposure of 10 min after 3 days
Hygroscopicity Moisture content:	≤ 5% ≤ 2%	GWP, ODP and ALT (Atmospheric Life Time) values:	negligible or zero effect
Vibration resistance:	No structural loosing, deformation or damage after test	Nozzle outlet temperature:	180~200 °C at 5 mm distance to the nozzle
Shock resistance:	No structural loosing, deformation or damage after test	Gas productivity:	≥ 300 ml/g

*Testing conditions and evaluation methods are regulated by GA 499.1-2004 and GA 499.1-2010.

DESIGN AND APPLICATIONS OF HOT AEROSOL EXTINGUISHANT

G1 Hot Aerosol System Design

The fire extinguishing dosage for G1 hot aerosol fire extinguishing agents can be calculated according to Eq. (7):

$$M = A R_e (1 + K) \tag{7}$$

where M is the dosage (kg); A is the cross-sectional area of the tank (m^2); R_e is the effective forming agent dosage per storage area of tank (kg/m^2) and K is the compensation coefficient.

Here R_e and K depend on tank type and diameter. See Table 7.

G2 and G3 Hot Aerosol System Design

A modern aerosol fire extinguishing system is composed of fire sensing, alarm, electrical ignition, and discharge units, aiming at fire extinguishing of multiple classes and is designed to be more portable and convenient in assembling, more stable for long-time standby and integrated into a local fire extinguishing network. See Figure 13.

Table 7: R_e and K value for G1 extinguishing system design. (Reproduced with permission from Duan *et al.*, 2007).

Tank type	Class I & II liquid*		Class IIIA & IIIB liquid*
	R_e for Fixed roof (kg/m^2)	R_e for Floated roof (kg/m^2)	R_e for Fixed roof (kg/m^2)
Out-tank	1.0	0.8	0.7
In-tank	0.8	-	0.46
Tank diameter (m)	**Compensation coefficient K**		
D≤10	0		
10<D≤15	0.1		
D>15	0.2		

*Class I liquid's flash point <37.8 °C, Class II liquid's flash point ≥37.8 and <60 °C, Class IIIA liquid's flash point ≥60 °C and <93 °C, and Class IIIB liquid's flash point ≥93 °C, Regulated by NFPA 30.
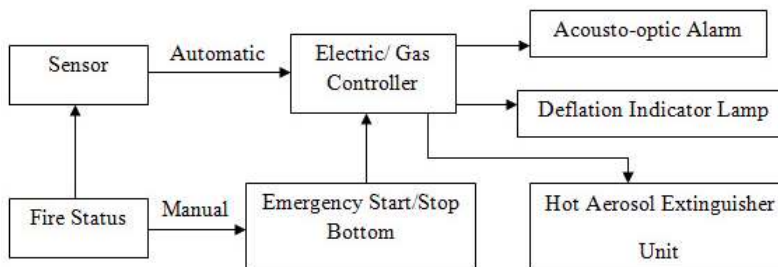
Figure 13: Integral blocks of hot aerosol extinguishing system.

The area or volume protected by hot aerosol extinguishant should be less than 500 m^2 or 2000 m^3. The working temperature for G2 and G3 hot aerosol forming agents ranges from -20~55 °C with relative humidity less than 90%, and the protected room should have an opening density less than 0.6%. If the opening density is larger than 0.6%, then blocking devices are needed to ensure a successful fire extinguish (DB 61/368-2005).

For K-type and S-type fire extinguishing agents, dosage for fire extinguishing in a confined area is determined by Eq. (8):

$$W = C_2 K_v V \qquad (8)$$

where W is the dosage (kg) and C_2 is the effective fire extinguishing concentration (kg/m^3) of aerosol forming agent, V is the volume under protection (m^3) and K_v is the volume correction coefficient. K_v and C_2 depend on fire types and the volume protected. See Table 8.

Areas Applying Hot Aerosol Fire Suppression Technology

Compared to other fire extinguishants, hot aerosol fire extinguishing agents have unique advantages, seen in Table 9. Especially, G2 and G3 hot aerosol fire extinguishing systems have been widely applied in places like communication basements, data analysis rooms, and transportation engine compartments, etc.

But because aerosol particles can have hazardous effects on human health, applications of hot aerosol technology are usually limited to areas like engine cabins, gas turbine cabins, machinery cabins, warehouses, electrical cabins, cable tunnels and computer data processing rooms, etc. where human activities are rare (Zhao *et al.*, 2004). See Table 10.

Table 8: C_2 and K_v values under different conditions*.

	Least C_2 for K-type	Least C_2 for S-type	Least K_v for K-type	Least K_v for S-type
Solid fire	0.1 kg/ m^3	0.1 kg/ m^3		-
Electrical fire	-	0.13 kg/ m^3		-
Tunnel fire or generator room fire	0.14 kg/ m^3	0.14 kg/ m^3		-
V< 500 m^3	-		1.0	1.0
500 ≤ V< 1000 m^3	-		1.1	1.1
V≥ 1000 m^3	-		1.2	1.2

*Data from DB 61/368-2005.

Table 9: Key Characteristics of Major Extinguishants in Market*.

Extinguishant	Halon	CO_2	FM-200	SDE	IG-541 Inergen	G2 & G3 Hot Aerosol
Min. extinguishing fraction (Vol. %)	5	34	8	8	36.5	30-200 g/m^3 (Hu, 2009)
Storage pressure (MPa)	2.5/4.2	5.17	2.5/4.2	≤ 1.6	15/20	0
LOAEL** (Vol. %)	7.5	> 20% Fatal	10.5	17.5	52	Low***
Fire extinguishing efficiency per cost	low	low	low	low	low	high
Developing prospect	out of date	limited	developed	developed	developed	developing

*Data from GB 50370−2005.**LOAEL stands for lowest-observed-adverse-effect level which means lowest concentration or amount of a substance found by experiment or observation that causes an adverse alteration of morphology, function, capacity, growth, development, or lifespan of a target organism distinguished from normal organisms of the same species under defined conditions of exposure.*** No dead mice found in a 1 m^3 compartment containing aerosol generated by 100 g of forming agent.

Table 10: Application Areas of Hot Aerosol Extinguishing Agents.

	Communication base station	Electric power industry	Petroleum industry	Spacecraft cargo room	Weapons warehouse	Mobiles engine room or oil tank	Metallurgy industry
G1			✓			✓	✓
G2		✓	✓		✓	✓	✓
G3	✓	✓	✓	✓	✓	✓	✓

COOLING AGENT FOR HOT AEROSOL FIRE EXTINGUISHERS

Hot aerosol forming agents generate a large amount of heat during redox and may cause secondary fire risks. The temperature of a hot aerosol discharge can vary from 600-1200 degrees Celsius at 1 cm distance from the nozzle of the canister (Song, 2003), so it is necessary to place coolant inside the extinguisher device.

Currently, there are two typical ways to place coolants. One is to mix coolants with aerosol forming agent ingredients (Qiao *et al*., 2001), and the other more common way is to place perforated metal plates, a beehive-like coolant block or granulized coolant pellets between the aerosol forming agents and the canister nozzle, separating coolants from the aerosol forming agent.

Cooling mechanisms can be physical or chemical. Physical methods cool down hot aerosol temperatures through pure heat absorption by perforated metal plates or metal bars (usually copper bars), but the physical cooling efficiency is low since metals have limited heat capacities. Chemical cooling methods involve the decomposition and phase change of coolants, which adsorbs a large amount of heat. Those coolants can be simple natural material like water containing minerals or simple chemicals like urea or aluminum hydroxide (Qiao *et al*., 2001) or synthetic composites which are thermally unstable. See Table 11.

Table 11: Hot aerosol extinguisher coolant.

	Physical	Chemical
Component	Metal bars, balls or perforated metal plates	Urea, aluminum hydroxide powders, marbles, synthesized materials, etc.
Cooling mechanism	Heat conduction & capacity	Phase change and decompose
Placement	Between aerosol forming agent and canister nozzle	Between aerosol forming agent and canister nozzle or mixed with aerosol forming agent
Performance	Limited	Remarkable (Zhang & Liao *et al*., 2006)

Coolant packing should have enough porosity to avoid blocking hot aerosol. If blocking occurs, explosion of the extinguisher due to a sudden pressure accumulation in the canister can happen.

For coolants mixed with aerosol forming agent ingredients, if an excessive amount of coolant is added, it may fail to ignite the hot aerosol forming agent. By mixing coolants, the redox rate of the hot aerosol forming agent will be decreased, so mixing is rarely adopted (Hu, 2003).

CONCLUSION

In this review, hot aerosol fire extinguishing mechanisms, agent ingredients, extinguisher devices, technical terms, applications and aerosol forming agent coolants are reviewed. Characteristics of hot aerosol fire extinguishing technology were compared with other common fire extinguishing technologies such as cold aerosol, inert gas, Halon and water mist. Basically, hot aerosol fire extinguishing agents have higher fire extinguishing efficiency than inert gas, Halon and water mist fire suppression technology with negligible ODP and GWP values, but health and visible impairment caused by aerosol particles and gases, together with the large amount of heat released during aerosol discharge, are problematic. The ingredients in hot aerosol forming agents are mainly oxidants such as nitrates or halogenic acid salts and reductants like carbohydrates, derivatives of guanidines and cellulose, carbon blacks and metallic powders. Additives in hot aerosol forming agents include binders, combustion adjusters, desiccants and surfactants. The choice of oxidants and reductants determines the type of aerosol forming agent and fire extinguishing behavior. Oxidants containing Group I elements are K-type and oxidants containing Group II elements are S-type. For fire extinguishing efficiency, nitrates are better than halogenic acid salts. Less hydrated oxidants are better than highly hydrated ones and reductants which can produce as much inert gas and water vapor as possible are preferable.

The hot aerosol fire extinguishing process is primarily based on recombination of fire supporting radicals with oxides and halides of metal elements,

together with an oxygen dilution and cooling effect caused by gases generated by aerosol forming agent combustion. Oxides are better than halides in fire extinguishing and Group I elements are better than Group II elements in recombination of fire supporting radicals, so K-type hot aerosol forming agents have higher fire extinguishing efficiency than S-type. This also reflects the smaller sizes and evaporation temperatures of K-type aerosol particles, but precipitates of S-type aerosol particles have much higher electrical resistivity which can prevent severe damage to electrical devices and electronics. For both G2 (K-type) and G3 (S-type) hot aerosol fire extinguishing devices, portable or fixed/attached structures are used. Fixed/attached hot aerosol fire extinguishing devices usually have a canister configuration. Portable types include hand-held and grenade types. For G1 (K-type) hot aerosol fire extinguishing technology, device configurations are in-tank or out-tank types. There are differences in technical terms and standards for G1, G2 and G3 hot aerosol forming agent post-extinguishing performances. Differences in their system designs are due to differences in their fire protection application and protection area characteristics such as volume, geometry or opening density. Both G2 and G3 hot aerosol fire extinguishing technologies have wide applications in many sites like engine or cargo compartments, warehouses, cable tunnels etc. On the contrary, G1 hot aerosol fire extinguishing technology is only applied for oil tank fire protection. Moreover, G2 hot aerosol fire extinguishing technology cannot be applied in places where delicate electronics, electrical devices or important archives are present. Though modern integrated hot aerosol fire extinguishing systems are highly automatic and efficient, their application is still limited to areas without human activities since hot aerosols can bring hazards to environment and human health. High temperature aerosols can be cooled chemically by phase changes and thermal decomposition of natural or synthetic coolants. The physical cooling effect is limited. Coolant packing or mixing should not cause clogging of aerosols or failure in ignition of aerosol forming agents.

NOMENCLATURE

I	emissions source for primary particles
J	particle size (m)
N	number of primary particles
M	number of particle sizes (m)
N	number concentration
R	number radius of particles

Q_s	scattering coefficient
Q_e	extinction coefficient
d_p	diameter of primary particles (m)
R_g	radius of gyration of an aggregate (m)
D_f	fractal dimension
k_f	fractal prefactor
N	terminal velocity of spherical particles (m/s)
P	density of particles (kg/m^3)
ρ_0	density of disperse medium (kg/m^3)
g	gravitational acceleration (m/s^2)
H	dynamic viscosity of disperse medium (Pa•s)
D	diffusion coefficient (m^2/s)
R	ideal gas constant (J/mol•K)
T	temperature (K)
N_A	Avogadro number
M	dosage (kg)
A	cross-sectional area of tank (m^2)
Re	effective forming agent dosage per storage area of tank (kg/m^2)
K	compensation coefficient
W	designed dosage (kg)
C_2	designed fire extinguishing concentration (kg/m^3)
V	volume under protection (m^3)
K_v	volume correction coefficient

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