Development of environmentally benign fire retardant coatings

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Abstract:

Urban population density has increased multi-fold in developing countries like India and China. Increased population density and changing life styles have resulted in situations more prone for fire hazards. Also, there is a growing concern and awareness among public as well as policy makers about issues related to fire safety. Fire retardant coatings play a vital role in reducing the flame spread rate and there by guarantee life safety during fire hazards. Research efforts in the recent past have led to the development of fire retardant coatings which are either halogenated or phosphorus based. Majority of these fire retardants are finding use in plastic industry. According to an estimate by OECD (1994), Organization for Economic Cooperation and Development (Paris) on worldwide demand for fire retardants in the year 1992 was about 600,000 tonnes and about 50% of this demand is met by halogenated and phosphorus based fire retardant chemicals. These materials are very much hazardous to the environment as well as to human health as they form corrosive and sensory irritants. Hence there exists a need to develop environmentally benign fire retardants.

This paper explores the possibility of deriving fire retardant coatings or fire suppressant materials from resources like fly ash, a waste generated from thermal power plants. Coating techniques and issues related to bonding will be explored. Experiments conducted using precipitated silica and related compounds in the form of silicates in fire retardant coatings have indicated a possibility of durable coating formation. This will be reviewed further to establish the socio-economic and environmental benefits of these fire retardants.

Key words:

fire retardant, fire suppressant, halogenated, non-halogenated, environment

1. Introduction

Increasing population and changing life styles of current world is one of the reasons to the increasing fire hazards. Fire hazards are heard frequently every year across the world causing a miserable situation to life and property. In India, Delhi fire service (1942), the country’s first fire service, responds to 15000 fire/rescue calls per annum with in the Delhi state [1]. According to a annual statistics by Andhra Pradesh Govt., the fire service has attended to 14802 calls costing property damages estimated at Rupees 888 crores and 167 lives in the year 2006 [2]. A statement provided by Karnataka State Fire and Emergency services, the department has responded to over 111681 calls of fire that has caused damages to property worth Rupees 3897crores and 6166 lives in the last eleven years (1999 to 2009) [3]. Further the major fires viz. Chennai - LIC building fire (11th July 1975), Chennai - Moore Market Fire (30th May 1985), Upahar Cinema Fire (13th June 1997), Kumbakonam school fire (16th July 2004) and the recent Bangalore - Carlton Tower fire (23rd Feb 2010) are major fire accidents in the Indian history. In all fire tragedies the rate of flame spread and smoke production are responsible for creation of untenable conditions in very short time. Smoke detectors and sprinklers, which are active in nature and act during the occurrence of fire, are the primary defense [4] during fires. Fire retardants postpone the onset of untenable conditions by reducing flame spread rate and smoke production providing valuable escape time for the affected persons.

The growing awareness of public and the government towards life and fire safety, has led to the introduction of more stringent codes with respect to fire and life safety. Fire protection systems provide additional protection from fires by increasing the escape time. The history of fire retardant development dates way back to 200 BC, when the Romans used a mixture of alum and vinegar on wood to prevent fire. Perkin has described a flame retardant treatment for cotton using a mixture of sodium stannate and ammonium sulfate in the year 1912.With the advent in the development of plastic technology, halogen and phosphorus based chemicals gained prominence. They were introduced by scientists as flame retardant additive to polymers [6]. A good blend of active and passive protection systems provide life safety during fire incidents.

2. Need for environmentally benign fire retardants

Fire retardants are chemicals that are used in plastics to reduce the flammability. According to an estimate by OECD (1994), Organization for Economic Cooperation and Development (Paris) on worldwide demand for fire retardants in the year 1992 was about 600,000 tones and about 50% of this demand is met by halogenated and phosphorus based fire retardant chemicals [6]. These materials are very much efficient as they take part in the free radical chain reaction of the combustion process. But they release toxic compounds to the environment and cause serious problems (carcinogens) to human health [5-6]. Further they also form corrosive and sensory irritants. The concern over the ozone layer protection and the subsequent call for banning chloro fluoro carbons (CFC) by the Montreal Protocol (16th September 1987), led to the quest for alternates for halogenated fire retardants [18]. Since then development of non-halogenated flame retardants has acquired prominence and there is growing evidence of focused research in this field.

3. Market trend for Halogen free fire retardants

A study report by Helmut Kaiser consultants [7], a German firm indicates that the demand for Halogen-free Flame retardants market will increase from 1.62 bn US $ in 2005 and to 2.72 bn US $ in 2010 worldwide. The impact is due to the public consciousness of the hazardous halogenated products, the industrial end-user initiatives and the environmental legislation. In China, Eastern Europe and other parts of Asia, the booming economy and the strengthened fire protection standards stimulate the market of fire retardants overall, from which the halogenated and non-halogenated products both benefit.[7]

4. Mechanism of fire retardants

Fire retardants are generally chemicals containing organic or inorganic species; act in five different ways viz. Gas dilution, thermal quenching, protective coatings, physical dilution and chemical interactions or through a combination of all these mechanisms [6]. These mechanisms are described below:

Inert gas dilution involves the production of large volume of non-combustible gases that dilute the oxygen supply to the flame or fuel concentration below the flammability limit. For example, Metallic Hydroxides, nitrogen compounds.

Thermal quenching is the endothermic decomposition of the flame retardant. This decreases the rate of burning. For example, Metallic hydroxides and nitrogen compounds.

Protective coatings involve either formation of char barrier or formation of liquid that limits in the flame front available to the combustible material. For example, phosphorus based intumescent coatings.

Physical dilution involves action of fire retardants as thermal sinks so as to increase the heat capacity of the combustible material or in the reduction of fuel content. For example, glass fibres, talc.

Chemical interaction involves in the interaction of fire retardants in inhibiting the free radical chain of combustion process. For example, halogenated and phosphorus based fire retardants.

5. Silica from Fly ash

Fly ash is a waste generated from thermal power plants and is of global concern. This paper attempts to explore the possibility of deriving fire retardant coatings or fire suppressant materials from resources like fly ash, a waste generated from thermal power plants. A typical composition of fly ash (Class F as per ASTM C618 standard) is given in Table 1. From Table 1, it is evident that the major portion of fly ash is characterized by silica, alumina and iron. Iron can be eliminated by means of suitable magnetic separation process, thus leading to an increase in concentration of silica and alumina. Silica and alumina can further be separated by Bayer's process followed by calcination. Silica and alumina are known to possess thermal stability and thus can be utilized in the development of environmentally benign fire retardants, as they are much safer than halogenated and phosphorus based fire retardants. This leads to effective utilization of fly ash. Thus we have the benefit of using a wasted resource.

Table 1: Typical composition of fly ash (class F) from Raichur Thermal Power Station

Parameter	%
Silica (SiO_2)	51.06
Alumina (Al_2O_3)	20.29
Ferric Oxide (Fe_2O_3)	10.82
Calcium oxide (CaO)	7.11
Magnesium Oxide (MgO)	2.32
Total Alkalis as (Na_2O equivalent)	0.25
Loss on ignition (LOI)	7.19

Table 2: Cone calorimeter data [10]

Sample	Residue Yield (%)	Peak HRR (kW/m^2)	Mean HRR (kW/m^2)	Mean H_c (MJ / kg)	Mean SEA (m^2 / kg)	Mean CO Yield (kg/kg)
Nylon 6	1	1010	603	27	197	0.01
Nylon 6 silicate nano composite (2%)	3	686	390	27	272	0.01
Nylon 6 silicate nano composite (5%)	6	378	304	27	296	0.02

Heat flux: 35 kW/m^2, H_c: Heat of combustion, SEA: Specific extinction Area, HRR: Heat Release Rate. Peak heat release rate, mass loss rate and specific extinction area (SEA) data measured at 35kW/m^2 are reproducible to within ± 10%. The carbon monoxide and heat of combustion data are reproducible to within ± 15%.

Efforts towards finding an alternative source to the halogenated and phosphorus based fire retardants has led to more intensive research by scientists due to which many new articles, patents and products related to eco-friendly fire retardants are published [10-17]. This includes the studies on different forms of silicon. Almost all forms of silicon have been explored as flame retardants. Fire retardant (FR) behavior of Si based materials has been studied for silicones, silica, organosilanes, silsesquioxanes and silicates. Levchik and coworkers[10] recently reported their investigation on the effect of the talc ($3\ MgO.4SiO_2.H_2O$) on the flammability properties of polyamide -6 (PA-6) flame retarded with ammonium poly phosphate. Bourbigot and Le Bras et al [10] have investigated the effect of variety of aluminosilicates on the performance of intumescent FR formulations. Studies on silicon based compounds have shown that the mechanism of these fire retardants follow a char enhancing mechanism which in turn acts like protective barrier to the surface on which they are coated. Table 2 shows the cone calorimeter data of silicon based fire retardant composites. From the cone calorimeter data given it is evident that addition of silica to the polymer shows improvement in their fire retardancy as indicated by their reduction in heat release rates by 30 to 60 percent with increase in silicate nano composite concentration of 2 to 5 percent. Further the increase in percentage residue yield indicates the retention of the material has doubled in fire situations with increase in nano silicate composite concentration. However there is no much variation with the heat of combustion, SEA, though there was increase in carbon monoxide yields noticed at 5 percent silicate nano composite concentration. This shows that there is formation of high performance char barrier forms with the introduction of silicon based compounds, and char barrier acts as insulator and mass transport barrier [10], thus reducing flame spread. This is the advantage of silicon based fire retardant and it can be made from recycling.

6. Coating Techniques

The efficiency and effectiveness of fire retardancy of a material unless otherwise it is inherent, depends upon the chemistry of coating technique. Different types of coatings are available in the literature, roller coating, knife coating, gravure coating for printing, rotary screen coating, hot melt coating and transfer coating are few to mention. There is also powder coating techniques involving Electron Beam spray coating techniques. All these coatings have been used for silicon based coatings. In this paper we have considered coating for fabric. Coatings used in the production of technical textiles are largely limited to those products that can be produced in the form of viscous liquid, which can be spread on the surface of a substrate. This is then followed by drying and curing process, which hardens the coating so that a non- blocking product is produced. Thus the coatings for these products are limited to linear polymers, which can be coated as polymer melt or solution and on cooling form a solid film or form a solid film by evaporation of the solvent. Coatings may also be applied in the liquid form and then chemically cross linked to form a solid film [19]. In this paper the authors have used a thermoplastic material poly vinyl alcohol (PVA), the polymer is water soluble at moderately high temperatures, say about 60° to 70° C. The silica solution and the polymer medium are prepared separately. The fabric fiber is first encapsulated using the polymer medium and then soaked in silica solution for longer duration thus enabling the silica particles get adsorbed over the surface of the fibre.

7. Bonding issues:

Silica is bonded to substrates of varying nature as reported in the literature. Coating techniques employed are found affect the bonding. The properties of coated substrates are likely to have altered physical properties. Bourbigot etal [10] reports that Ethyl Vinyl Acetate (EVA) has a 35% lower elongation break, when formulated with a mass fraction of 30% silane treated aluminium trihydrate (ATH).Adherence of coating to substrate might have mechanical issues. Hence it is important to check the integrity of the coating with respect to number of washes, repeated ironing, etc. in the case of fabrics. Further, the coating must not alter the appearance significantly. The choice of silica as fire retardant additive will be required to address these bonding issues.

8. Experimental study

Table 3 shows the data obtained in a study conducted on fire retardancy of fabrics, two samples of FR fabric from the market (M/s. Ahill Roopa stentering, Coimbatore and M/s.Giri textiles, Bangalore) along with the coating developed by the authors. The intent of the study is to check the flammability rate of these fabrics in comparison with the untreated fabrics. Fig 1, 2 & 3 shows the image of the flammability.

Fig. 1: FR fabric from Ahill Roopa

Fig. 2: FR fabric from Giri Textiles

Fig. 3: Fabric Coated at CDM, JU

Table 3. Flame Retardancy Study

7/7/2010 Date of conducting the study:06/7/10

S.No	Sample	Ignition point			Flame Spread	after glow	Residual Mass			Remarks
		start	stop	duration	time(s)	(s)	Initial (g)	Final (g)	% Residue	
1	Untreated fabric	14	20	6	37	totally burnt	1.31	0.342	26%	5sq.cm curtain piece from vertical blinds used in all
2	Treated fabric-1	0	15	15	53	3	1.698	1.116	66%	coated with 1%PVA and 5% silica soaked for 24hr
3	Treated fabric-2	0	16	16	67	24	1.829	1.106	60%	coated with 1%PVA and 5% silica soaked for 1hr
4	fabric from Ahill Roopa stentering	Not ignitable			No flame spread	only charing upon flaming	0.458	0.392	86%	stentered fabric
5	fabric from Giri Textiles	Not ignitable			No flame spread	only charing upon flaming	0.95	0.5	53%	

Note: Samples were prepared on 29/6/10 and were allowed to dry naturally.

Solutions of 1% poly vinyl alcohol (PVA) and 5% silica are prepared separately. The silica used is extracted in-house from flyash of Raipur Thermal Power Station, Karnataka. Three weighed samples of 5cm x 5cm curtain fabric were prepared. Two of them were soaked in the prepared solutions of PVA and silica separately for 1h and 24h respectively ensuring the encapsulation of fabric fibre using the polymer medium and then soaked in silica solution for longer duration enabling the silica particles get adsorbed over the surface of the polymer. The samples were dried and weighed. Two FR fabric samples from market were also prepared. They were tested for flammability using Bunsen burner flame by appropriately hanging them vertically on a burette stand. The convective heat transfer coefficient and the flame temperature were regressed to be 26 $W/m^2/K$ and 973 K, respectively, which corresponds to an initial convective heat flux approaching 48 kW/m^2 [20]. The samples were then compared with the untreated fabric. All fabrics, were found to show resistance to ignite, and upon ignition showed resistance to flame spread. The treated samples, Treated fabric-1 & 2 were found to match the performance of the market samples with regard to flame spread. The untreated fabric got ignited in 6 seconds and got totally burnt by 37s. Further, increased soaking of the medium into the fire retardant medium showed increased absorption over the fibres and reduced the afterglow. The study conducted gave encouraging parametric values and more parameters relevant to heat release rate, soot characteristics, will be studied further to evaluate the suitability of the medium as fire retardant coating to fabrics.

9. Conclusion

Fire retardancy of silica and related compounds is found to be well established by many researchers around the world. Further the material's ability to act as protective layer or insulating material to the surface is also well established. Existing process of extracting silica flyash and the flyash characteristics shows evidence to possible derivation of fire retardant coatings or fire suppressant materials from fly ash. Experiments conducted using precipitated silica and related compounds in the form of silicates in fire retardant coatings have indicated a delay in ignition time 16s and slow flame spread up to 67s and loss of residue to 66% of the market fabric which is comparable to the existing FR fabrics from the market which are ranging from 53% to 86% as according to similar study. This shows a possibility of durable coating formation. In this connection, coating techniques and issues related to bonding are explored so as to facilitate their usage in fabric coatings as well.

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