FIRE SAFETY SCIENCE

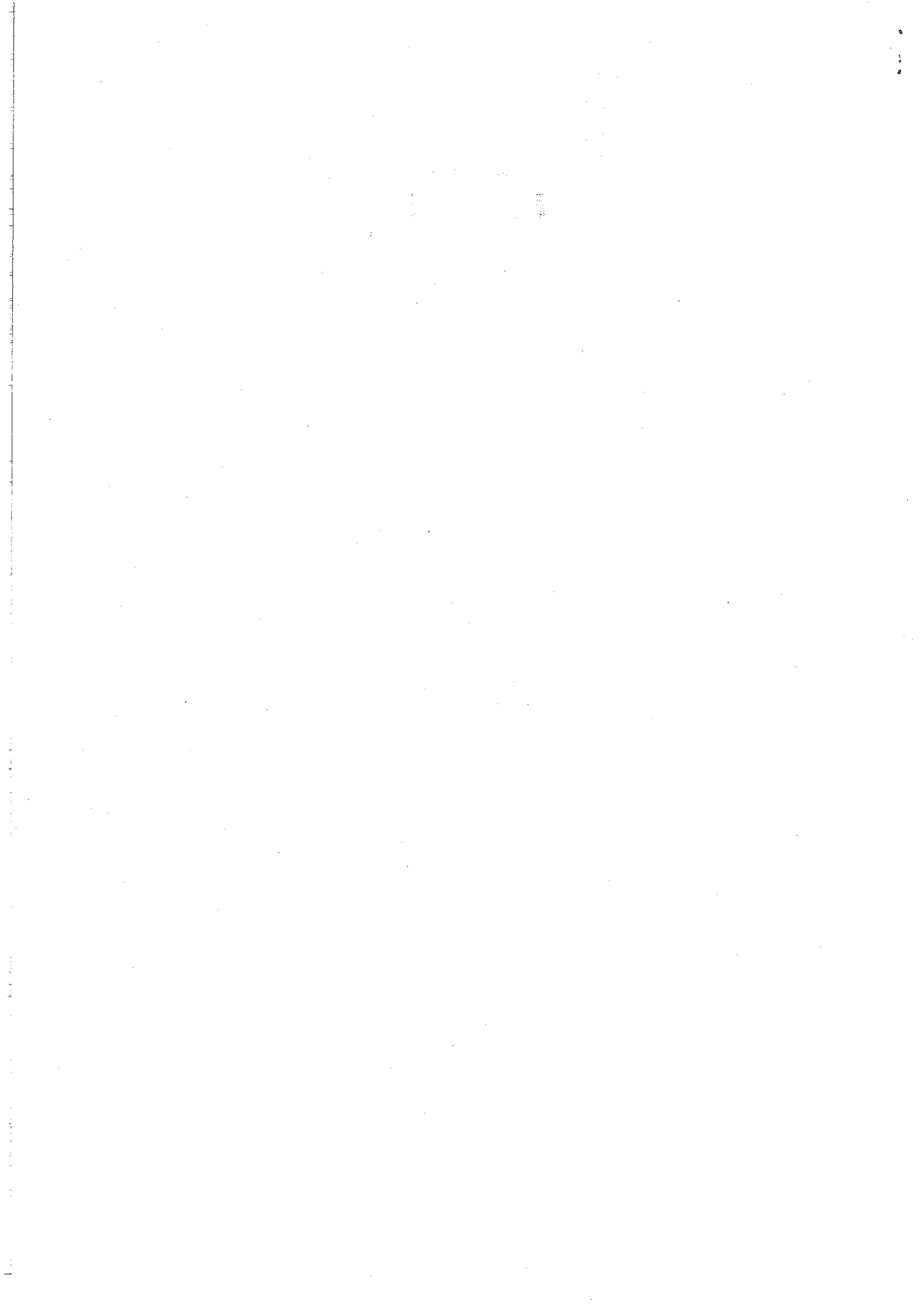## An International Journal

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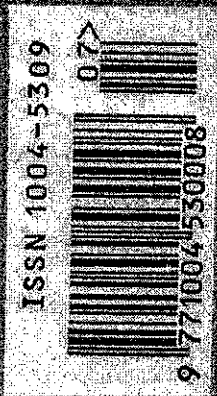
Smoke Suppession in Poly (Vinyl Chloride)

Sunil K. Sharma

(Fire Research Central Building Research Institute ROORKEE (UP) 247 667　India)

S. K. Srivastava

(Chemistry Department　University of　Roorkee ROORKEE (UP) 247 667　India)

ABSTRACT

Polymeric materials are combustible in nature and poly (vinyl chloride) is no exception. Due to its high chlorine contents it is relatively flame retardant, however because of the processing aids such as plasticizer etc. this advantage is lost. During burning the two main hazards of PVC are Hydrogen Chloride gas and copious amount of smoke. Different methods for smoke suppression of polymers are also applicable to the case of PVC. Complexes of different metal, mixed metals and metal based organics are discussed along with other methods of smoke suppression in PVC. Some aspects of smoke measurement have also been covered.

Key Words: *Smoke Suppressants, PVC, Metal Based Complexes, Additives, Fillers and Smoke Measurement.*

1. Introduction

The cost of fires in the developed world is increasing considerably as more and more synthetic polymers are replacing the traditional materials both on the domestic and the industrial scene[1]. The growth in use of synthetic polymers is , unfortunately, associated with a dramatic increase in the number of serious fires, number of deaths and injuries in fire. Organic polymers tend to ignite and burn when exposed to an ignition source. The principle danger of such an exposure is the emission of smoke and toxic combustion products. Though the combustion gases are the leading cause of death, several studies have shown that intense levels of visible smoke may precede the formation of excessive quantities of toxic combustion products[2]. Smoke poses a danger to human life, particularly in the initial phase of fire, due to disorientation by light obscuration and scattering effects of gases and particulates. Loss of visibility accompanied by panic conditions, prevent or delay the escape of occupants untill toxic gas concentration and temperature become critical. Smoke inhalation and not the fire itself is the killer that accounts for majority of fire deaths[3]. Smoke from burning polymers is generally the result of incomplete combustion. The most common component of polymer smokes are carbonaceous and aqueous compounds. The main obscuring effect of smoke however is due to its carbonaceous particles i. e. soot[4].

Synthetic polymers represent one of the major fire hazards, particularly since, these generate large volumes of smoke and toxic gases during combustion. Reduction in smoke forming tendency of a polymer will thus increase the safety limit by allowing the fire victims additional time to escape. Most of the combustible materials do not meet the fire safety requirements. Use of fire retardant chemicals is thus necessitiated. Although several fire retardant systems have been developed for use in organic polymers, many of these are known to increase the amount of smoke and toxic gases generated by the polymer when it burns[1, 2, 5-7]. Since these combustion products are

known to be the major cause of deaths in fire, the use of smoke suppressants along with the fire retardants i. e. fire retardant smoke suppressant systems (FRSS) is the practicle solution to this problem. Though, the chemical treatment of materials to improve fire resistance can be traced back to eighteenth century, the smoke suppression has recieved attention only recently[2].
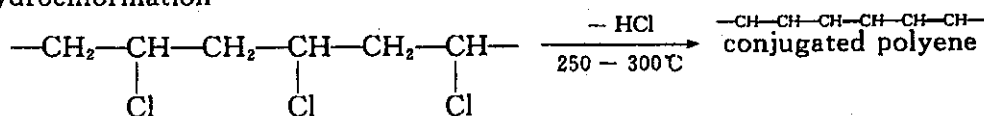
The term smoke has a vague definition. In general use, smoke is considered to be a cloud of particles, individually invisible, which is opaque due to the scattering and or absorption of visible light[8]. ASTM has defined smoke as an aerosol constituted of molecules of the gaseous products, the liquid droplets and the solid particles, formed during thermal decomposition of a material or during combustion[9]. The solid particles correspond to incomplete combustion. Hilado has related the phenomenon to combustion and introduced the aspect of gaseous products[10].

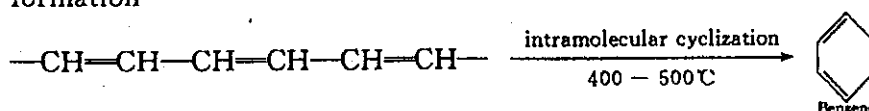## 2. Polymer Combustion Process

The three stages necessary to initiate the combustion process in plastics are : heating, decomposition and ignition of the polymer. The solid plastics tend to soften or melt and start flowing when heated by an external heat source, initiating decomposition of the polymer into volatile organic fragments. Decomposition is an exothermic process requiring sufficient energy to overcome the bond energy between individual atoms and to provide any necessary activation energy. The flammable gases formed during pyrolysis mix with atmospheric oxygen to result in ignition. Heat from these exothermic radiated is back to the polymer surface to increase the temperature of the pyrolysis zone, resulting in an increase in decomposition and production of combustible organic fuel (Fig 1).

In presence of sufficiently intense heat a polymer will pyrolyse breaking down to low molecular

Radiation (heat flux from flames to surface)

Volatile organic fragments (mass flux from fuel to flames)

Figure 1   Schrmatic of Combustion Process

weight species. These species, in the dispersed phase, comprise the smoke in the absence of flame. At high heating rates and with ignition, these low molecular weight species fuel the polymer falme. In the absence of sufficient oxygen, solid smoke constituents are formed at higher temperatures particularly in the form of soot in the flame zone. One of the best known path of soot formation from polymers is as follows[11].

a) dehydrochlorination

$$—CH_2—CH—CH_2—CH—CH_2—CH— \xrightarrow[250-300℃]{-HCl} —CH—CH—CH—CH—CH—CH— \text{ conjugated polyene}$$
$$\quad\quad |\quad\quad\quad |\quad\quad\quad |$$
$$\quad\quad Cl\quad\quad\; Cl\quad\quad\; Cl$$

b) benzene formation

$$—CH=CH—CH=CH—CH=CH— \xrightarrow[400-500℃]{\text{intramolecular cyclization}} \text{Benzene}$$

Lattimer and Kroenke[16] described the formation of light aliphatic hydrocarbons and compounds with aromatic substitution, accompanied with more heavy compounds, having molecular weight in the range of 1000 to 2000, which are easily condensable. They have also proposed a mechanism of thermal degradation for PVC (Fig 2).

The proportion of different aromatics however, depends on the conditions of pyrolysis. The cleavage of the polyene chain results in simultaneous formation of benzene and HCl at 240℃[17]. A slow heating favours the intramolecular process and a high temperature flash pyrolysis favours
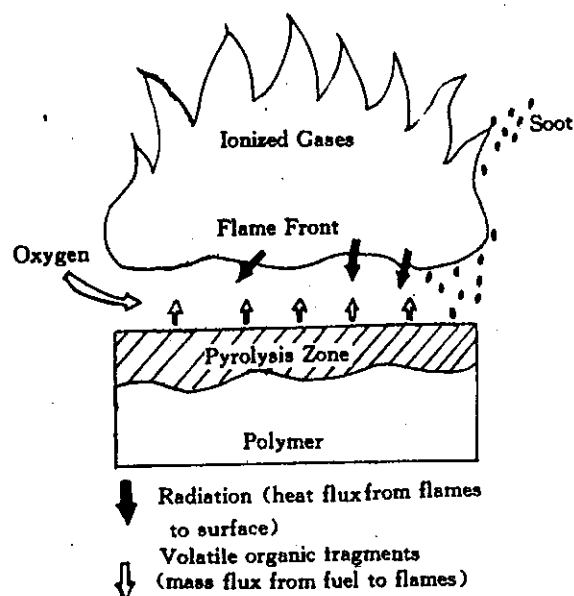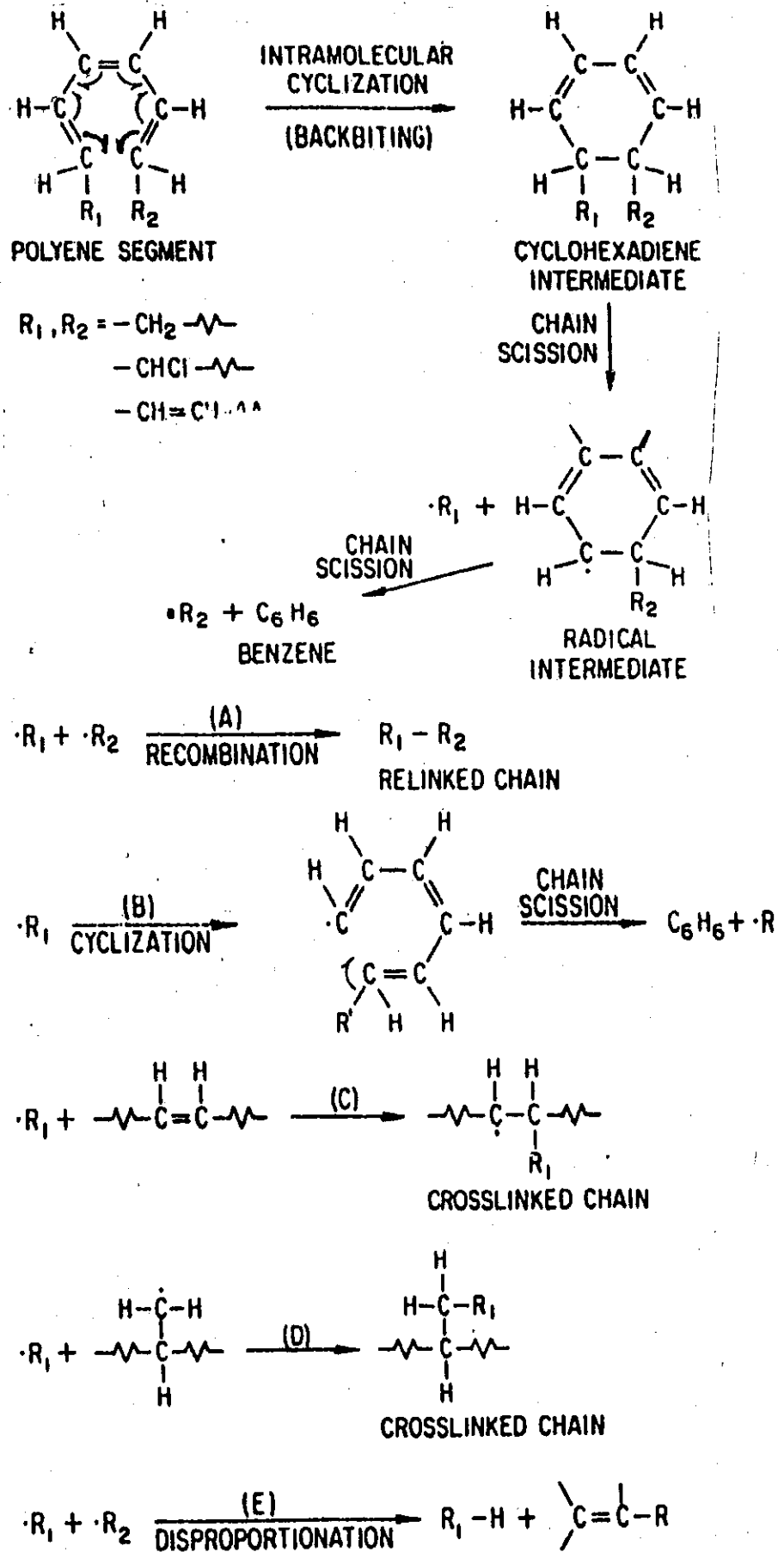
Figure 2　Thermal Degradation of Poly (Vinyl Chloride)

the intermolecular process. Some authors have proposed a Diel—Alder type of condensation between polyene chains, to account for the crosslinking which occurs rapidly during the thermal degradation of PVC. This mechanism has also been considered as an alternative process for the formation of benzene. However, according to O'Mara intramolecular cyclisation is the only mechanism which accounts for benzene formation and modifies the evolution of pyrolysis products. Pyrolysis below 300°C corresponds to almost complete dehydrochlorination accompained by degradation of the residue giving mostly benzene, the amount of which is limited to less than 3%[18]. The second step takes place above 300°C and corresponds to further decomposition of solid residue liberating carbon monoxide and carbon dioxide (CO and CO_2). Liberation of these compounds results in oxidation of the chain and a real combustion without flames of the carbonaceous residue, left after dehydrochlorination of PVC, takes place. Simultaneously the macromolecular chain scission takes place and smoke is evolved.

When the organic products issued by pyrolysis are in sufficient concentration, auto igition of the mixed gases takes place. Combustion of the polymer is accompanied by rapid release of CO and CO_2. The quantity of smoke formed in these conditons is very important.

4. Pyrolysis and Combustion — plasticised PVC

In majority of cases , PVC is utilized in the form of mixture with several constituents which are incorporated in the resin with the objective of contributing a particular property. The plasticized PVC may be considered as a mixture of homopolar melted in the presence of a plasticizer. Plasticizers are generally the esters of dibasic or high boiling point aliphatic or aromatic acids and are used in the range of 40 to 100 phr (parts per hundred parts of resin). This decreases the amount of chlorine available from the plasticised PVC. Plasticizers eg DOP{the most commonly used plasticizer for PVC (ethyl —2 hexyl phthalate / dioctyl phthalate)} are readily flammable. Thus the resultant PVC has poor fire resistance. Addition of 80 phr of DOP to PVC renders it flammable even under atmospheric conditions. Decomposition products of PVC include the products contributed by each of its constituent. The HCl liberated by the polymer modifies the decomposition process of DOP.

Since the plasticizer increases the degree of flammability of PVC it becomes essential to incorporate some fire retardnats in the mixture. However, as already stated the addition of fire retardants lead to increased smoke generation, thereby making it essential to look for an optimum solution. Lawson has reported the use of flame retardants having low levels of smoke emission[19].

5. Comustion and Smoke Generation

The mechanism of combustion of a polymer substrate involves application of an external heat source susceptible to liberate combustion products. These are then mixed with air and combustion takes place. For continuity of the pyrolysis it is essential that the heat produced by flames is transferred to the surface of the polymer. The volatile products diffuse into the flame zone introducing a radical chain process. Considerable amount of carbon may be formed during the combustion, some of which is deposited in combustion region as char while the rest is released as finely divided particles i. e. soot[20]. Soot forms a significant proportion of smoke. While smoke poses hazards to life, char is free from these, thus a potential method of decreasing soot formation is generation of additional char.

Soot is derived from volatile decomposition products of polymers. Thus the chemical structure of polymers is an important parameter in determining the relative amount of soot produced by different polymers under similar conditions of exposure[20]. Aromatic hydrocarbons lead to the formation of greater amount of smoke as compared to the aliphatic hydrocarbons. In view of this, the benzene formation during the pyrolysis of PVC appears to constitute an important intermediary in the formation of smoke. Polyacetylenes dominate among the combustion products of aliphatics while polycyclics are found in large quantities in case of aromatic compounds.

5. 1   Smoke From Polymers

The formation of smoke from polymers is considered as a case of pyrolysis or combustion of hydrocarbons. Three distinct steps are involved in soot formation: nucleation, growth and agglomeration. First the temperature of the polymer surface reaches 300 to 600℃, the temperature at which the degradation and liberation of gaseous products take place. The temperature of gaseous products then increases and its constituents are pyrolysed. At a significantly higher temperature the mixture is ignited and liberates the necessary energy for continuation of the process. The pressence of soot in a flame is the result of the fact that the rate of reactions forming solid carbon is greater than the rate of reaction which removes it. The amount of soot finally present varies strongly with the Carbon\Oxygen ratio and is heavily dependant on the type of fuel[21]. The condensed phase is composed of the origional polymer covered by a region of semi decomposed polymer which is, in turn, covered by a charry layer. The zone corresponding to the formation of volatile decomposition products from the semi decomposed substrate is the interphase and it is here where most of the initial reactions take place, particularly the action of additives such as flame retardants and smoke suppressants. The different stages involved in polymer combustion are[22] shown in Fig 3.
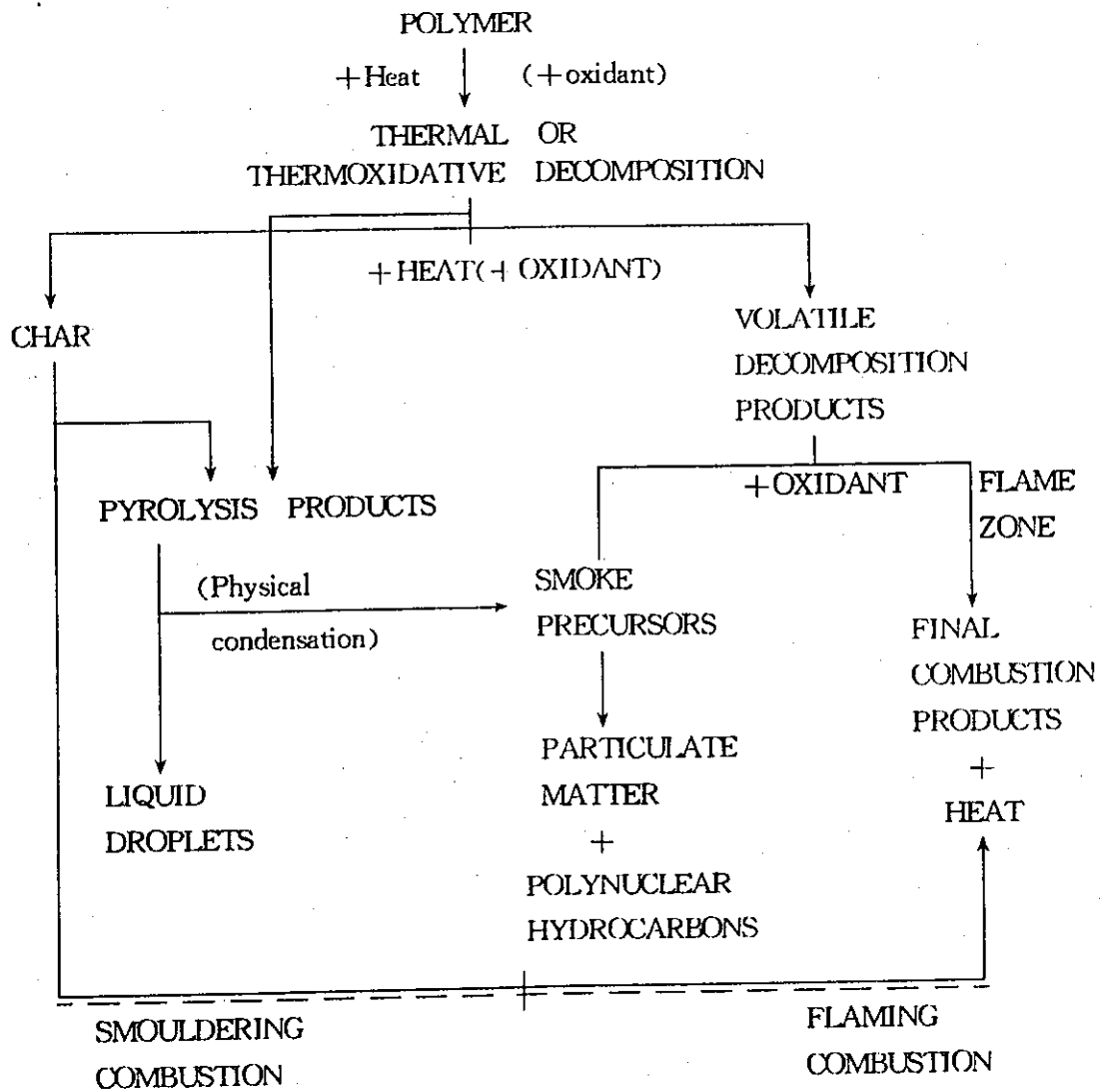

Figure 3 Different stages Involved in Polymer Degradation and combustion

PVC decomposes by a chain stripping mechanism to leave a polyene backbone. It is the polyene structrure which gives off abundant soot via the production of cyclic (mainly aromatic) hydrocarbons. In flaming combustion of PVC, after the dehydrochlorination further thermal decomposotion occurs resulting in small aliphatic hydrocarbons which gradually build up to soot or polycyclic aromatic hydrocarbons[22]. while the major part of smoke in smouldering combustion is from tars formed from the vaporisation of char residue, soot is the main cause in the flaming combustion[18]. Amount of char is more in non flaming combustion while it may be converted to CO and CO_2 depending on time and temperature available in case of flaming combustion. According to many authors the smoke generation during pyrolysis of PVC is due to the presence (among the products of degradation) of aromatic compounds and in particular the benzene. Smoke formation appears to occur after the dehydrochlorination process. Since the evolution of benzene is concomitant with the dehydrochlorination, it is probable that the smoke is not directly related to the benzene formation[15]. A general correlation between benzene reduction and smoke reduction however does exist[15]. According to Liebman[2] during the pyrolysis an increase in the amount of chlorine from PVC accompanies the inerease in benzene chloride and simultaneously a decrease in the quantity of benzene and smoke. In case of plasticized PVC formulations, degradation of plasticizer and formation of HCl play an important role in the formation of smoke during the thermal degradation of plasticized PVC[23]. A strong correlation exhists between the amount of plasticizer and the amount of smoke production during burning of PVC plasticized with bis {2ethyl hexyl Phthalate (DOP)}[24].

Solid particles such as carbon or inorganic fillers can act as soot forming nuclei. In addition to soot some hygroscopic fillers also increase the smoke density by triggering condensation of atmospheric water vapours.
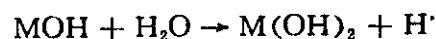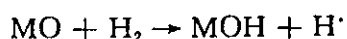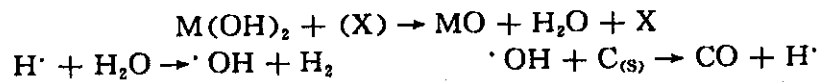
6. Smoke Supperssant

Having recognised the problem of smoke, there are essentially two ways of dealing with it. The first is to select materials which generate low quantities of smoke and the second is to modify those that do, either by chemical means or by the use of additives, so that the smoke generation is significantly reduced. In many polymer applications the first apporach is of limited use , since the polymer has been selected because of its very advantageous properties and there is often no low smoke producing substitute available. Since chemical modification is likely to be expensive the use of additives is the only viable means of reducing the quantity of smoke that would be generated in the event of fire.

6. 1 Additives

Earlier work on smoke suppressant (SS) treatments was directed at additives for reducing particulate emission from burner fuels; some of this work has been reviewed by Salooja[2]who has reported that the predominant class of additives for fuels are metal salts and complexes. The suppression of visible smoke from polymer combustion is always a consequence of soot suppression[4].

Many compounds, being used as smoke suppressant additives are suggested in literature[2, 25−28]. These can be classified as fillers, additives and intumescent coatings. Out of these , it is the additives that form the most widely applicable and diverse group. Additives are generally non polymeric compounding ingrediants, typically used at levels below 20% of the polymer mass. Essentially all of the reported SS additives for PVC have one thing in common, these are either metals or metal complexes. However, the non metallic additives may include carboxylic acids, aldehydes, alcohols, fluoroborates and sulfur etc. Iida and Goto[29] have reported 33 metal oxides and 23 metal chlorides as smoke suppressants. The metals appear to function as smoke suppressants through gas phase destruction or the prevention of formation of soot particles. A general mechanism for destruction of solid carbon in the dispersed phase has been proposed by Jenkins[2] as follows:

$$MO + H_2 \rightarrow MOH + H^{\cdot} \qquad\qquad MOH + H_2O \rightarrow M(OH)_2 + H^{\cdot}$$

$$M(OH)_2 + (X) \rightarrow MO + H_2O + X$$
$$H\cdot + H_2O \rightarrow \cdot OH + H_2 \qquad \cdot OH + C_{(S)} \rightarrow CO + H\cdot$$
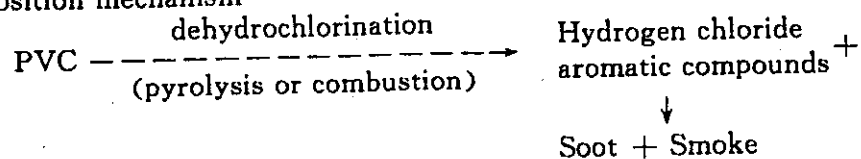
· These seem to be catalysts for the intermolecular reactions. The mechanism suggested for these reactions are: Diel—Alder reaction between polyene and chlorinated structures and Friedel —Craft alkylation of polyene and aromatic structures[18]. Two important reviews on smoke suppression of rigid Poly (vinyl chloride) by means of a large variety of metal compounds are by Kroenke[26] and Bert et al[27]. According to Kroenke[26] most of the smoke suppressants are not useful in commercial PVC compounds on account of availability, cost, colour, processing problems, stability and compatibility with the polymer. An effective SS may contribute in vapour phase condensed phase or in both via different processes eg dilution of fuel, modification of pyrolyzates, promotion of char formation or surface insulation etc. Transition metal oxides are oxidation catalysts and act as SS in varying PVC compositions. The efficiency is not very much dependant on the anion bound to the metal, but may depend on the temperature. These suppressors cause incandescence phenomenon along with complete and exothermic combustion of the solid residue without excessive smoke production[27]. A review of all the existing theories on the mode of action of smoke suppressants in PVC has been given by Fritz[30].

The comprehension of the mode of action of the additives and the mechanism associated with the decrease in quantity of benzene has been reported in numerous works and different explainations have been advanced. The benzene formatin by intramolecular condensation will be able to result in the thermal activation of electrons from polyene sequences formed by dehydrochlorination of PVC. Bert et al[27] have reported that though smoke reduction is parallel to the amount of benzene produced during pyrolysis, the correlation is not very precise.
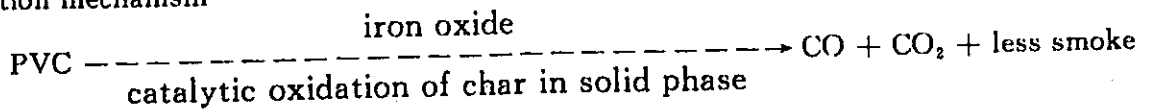
6. 1. 1 Iron Compounds

Ferrocene (dicyclopentanedienyl iron) was one of the first additive for which both flame retardance and smoke suppression (FRSS) was claimed[31]. 0. 4% content of ferrocene in PVC, significantly reduces smoke and enhances char formation. It acts both in vapour and condensed phases. Ferrous, ferric and ferricenium chloride were all shown to suppress the formation of benzene and smoke from PVC. Ferrocene may however be lost from PVC on ageing[15]. Its use is almost limited because of colour and high vapour pressure and is not recommended for plasticised PVC. Iron (III) oxide is a major SS formed from ferrocene and probably acts by reducing benzene formation and enhancing formation of oxides of carbon[14]:

Normal decomposition mechanism

PVC $\xrightarrow[\text{(pyrolysis or combustion)}]{\text{dehydrochlorination}}$ Hydrogen chloride + aromatic compounds

$\downarrow$

Soot + Smoke

Oxidation mechanism

PVC $\xrightarrow[\text{catalytic oxidation of char in solid phase}]{\text{iron oxide}}$ CO + CO$_2$ + less smoke

The action of Ferrocene is explained by transfer of energy in the triplet state preventing the activation of electrons[32]. Fecl$_3$ produced by the reaction of ferrocene and HCl at 200°C acts as a lewis acid, catalysing the dehydrochlorination and crosslinking of PVC[19]. Lawson has suggested a gas phase mechanism for smoke inhibition by ferrocene[19], while Descamps et al have suggested a condensed phase oxidation reaction visible as glow and leading to pronounced evolution of CO and CO$_2$. Catalytic oxidation of char to CO and CO$_2$ is also reported by Michel et al[33]. Guyot et al[18]have observed that ferrocene has a reverse effect on smoke suppression beyond 300°, while Bert etal[27] have reported a significant decrease of solid residue above 400°C. Carty et al[23] have presented a review on the role of iron containing compounds in char formation and smoke suppression when used in PVC formulations. Involvement of reactive intermediates derived from a range

of inorganic and organic metllic iron compounds in the overall reactions are proposed.

6.1.2 Molybdenum Compounds

Molybdenum oxide (MoO_3) when used in PVC exhibits smoke suppressant properties. Although the flame retardant effect of MoO_3 is slightly less than sb_2o_3[34] partial replacement for Sb_2O_3 by it results in fire retardance and smoke suppression. MoO_3[16] causes the PVC chains to become extensively crosslinked very easily in the degradation process. Therefore volatile pyrolyzate formation has to occur via multiple cleavage or crosslinked chain rather than by intramolecular or simple intermolecular reaction. Thus a smaller amount of volatile pyrolyzates are formed, char is enhanced and smoke is suppressed. MoO_3 has been reported to function as a lewis acid and reduce the formation of benzene by increasing the formation of aliphatic products in preference to aromatics during thermal degradation of PVC, probably via chemisorption reaction in condensed phase. Trans polyene segments which do not cyclise to benzene are the main products[35]. Relatively stable benzene—MoO_3 complex which suppresses smoke has been reported by Lum[36], while other results suggest a reductive coupling mechanism[16] which takes place as follows:

$$R\text{-}Cl + Mo^n \longrightarrow [R - Mo^{n+2}\text{-}Cl] \xrightarrow{[R'-Mo^{n+2}-Cl]} R\text{-}R' + 2Mo^{n+1}Cl$$
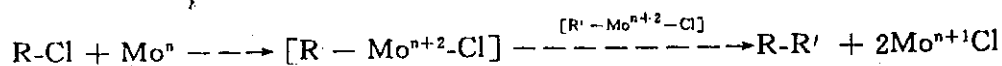
Combination of MoO_3 and Sn (IV) oxide is a synergestic FRSS in PVC and acts in condensed phase[26, 16]. Skinner and Haines[6] have reviewed the use of molybdenum compounds as FRSS in halogenated polymers and have reported a condensed phase mechanism. They have reported the usefulness of molybdenum compounds both in the rigid and the plasticised PVC. A combination of MoO_3 and aluminium trihydrate (ATH) was also found promising. Kroenke[26] has reported a synergism when MoO_3 was used in combination with certain compounds of copper, iron and tin. A review on the mechanism of molybdenum compounds acting as FRSS and their interaction with polymer substrate has been presented by Moore[37].

6.1.3 Zinc Compounds

Virtually any compound which will generate ZnO is a smoke suppressant for PVC[38]. Although zinc oxide has very effective smoke suppression properties, it tends to degrade PVC at elevated temperatures[14]. Many zinc compounds may however have unfavourable effects on polymer stability. Smoke suppressant effects appear to be optimum at 1 phr or lower. Some proprietory zinc based formulations eg ONGARD I , II and Firebrake ZB are known. Ongard II is a synergistic FRSS in PVC when used with Sb_2O_3[39]. Zinc compounds are reported to reduce the formation of benzene during pyrolysis of PVC[16]. Zinc oxide, combinations of zinc borate—ATH, and zinc borate—Sb_2O_3— $Mg(OH)_2$ result in strong smoke reduction with improved flammability by promoting strongly the formation of char especially in presence of ATH[40, 41] Moore and Kennely have reported use of zinc borate with other additives such as ATH, $Mg(OH)_2$· amm. molybdate, brominated phthalate and phosphate esters[42]. Highly flame retarded formulations can be prepared by using zinc borate with ATH or magnesium compunds as a replacement for the usual $CaCO_3$ filler[43].

6.1.4 Tin Compounds

Cusack and Smith[44] have reviewed the use of tin compounds in a number of synthetic polymers. SnO_2—MoO_3 combination has been reported to be synergistic smoke suppressant in rigid PVC[26, 45] Zinc hydrostanate and zinc stanate reduce the amount of carbon monoxide generated as well as act as FRSS in brominated polyester. Tin additives are active primarily in condensed phase and alter the pyrolysis of halogenated polymer by promoting the loss of halogen and enhancing cross linking to give an increased yield of char with a concomitant decrease in the generation of volatile flamable products[46]. In halogenated systems, the vapour phase — free radical scavenging action of evolved hydrogen halide may be assisting the presence of mist of fine tin oxide particles inflame. These provide the third body site for radical re—combination[47]. Tin compounds show significant smoke suppression even in unsaturated polyesters[48]. when used in conjunction with additive type halogenated compounds such as paraffin wax and deca bromdiphenyl

oxide[49, 50].

6.1.5 Other Metal Compounds

Essentially all of the effective metal based smoke suppressants appear to work in solid phase and interfear with the normal degradation pattern of PVC[5, 16]. Almost all the effective smoke retardants form char. ZnO, Fe_2O_3, most of the chlorides except CuCl and a number of acetylacetonates (Co, V, Fe) accelerate the initial polymer degradation while Cu and Ni compounds, TiO_2, MnO_2, Sb_2O_3 and MgO have little or no effect on the initial degradation of the polymer[27]. PVC containing 9.3% Cu_2S bound on it's chlorine group has been shown to generate no smoke at all[50]. Most efficient elements are Cu and Fe followed by Mg and Al and then the sequence Mn, Zn, Sb, Ni, V, Co, and Cr. Acetylacetonates are most efficient which can be ascribed to better miscibility of these organometalic compounds with a polymer[27]. Sharma and Srivastava have reported the use of chromium($\mathbb{II}$) acetylacetonate in plasticized PVC[51].

Most of the additives cause an increase in the rate of smoke generation, although the total amount of smoke is markedly reduced[27]. The amount of solid residue decreases greatly with the most efficient additives. Visual observations show clearly that incandescence is occuring indicating that the additives cause a more gentle combustion of residue without smoke. This is possibily caused by an active oxidation catalyst which results from the interaction of the additives and HCl. Additives including Cr_2O_3, MnO_2, Sb_2O_3 and some copper derivatives and HCl. Additives including Cr_2O_3, MnO_2, Sb_2O_3 and some copper derivatives lead to higher amount of CO and CO_2 as well as CO/CO_2 ratio.

Kroenke[26] has reported that of the pre—transition metals only the compounds of magnesium are useful as smoke suppresant for PVC; alkali and alkaline earth compounds are not effective. Magensium oxide and hydroxide have significant smoke reducion ability which may be because of the formation of oxichlorides at elevated temperatures. Antimony compounds have also been reported as SS for PVC[36]. These are mainly reported as part of mixed metal systems. It is possible that other compounds e. g. MoO_3 are responsible for most of the observed smoke reduction. Commercially modified antimony oxide e. g. Timonex[52] is claimed to act as SS in PVC. A few compounds of titanium and zirconium[53] have also been reported to be quite effective. Vanadium penta oxide also serves the purpose[27] probably because it is readily reduced. Chromium compounds have also been used[27, 36, 54]. As a class, the compounds of Cu are most effective as SS for PVC[26], Very strong smoke suppressing effects have been achieved in a number of cases by combining two or more metals in an active system e. g. iron powder+ cuprous oxide or molybdenum tri oxide; zinc and molybdenum compounds etc.

Concentration of the metal compounda has also a role to play. Relatively low concentration of wide variety of metal oxides particularly those of Al, Mg, Mo, Sn have been found to suppress soot formation effectively in halogenated organic compounds[4, 55]. If the loading of MoO_3 is increased from 2 to 10 phr a continuous reduction in smoke formation is observed, however this relation holds over a limited range of concentration. Similarly an increase in zinc oxide concentration beyond 1 phr exhibits a significant decrease in it's performance as SS[26].

6.1.6 Metal Based Organic Complexes or MBO

They cause incandescence of char residue left after dehydrochlorination in the temperature range of 350 — 450°C. This phenomenon parallels quantitative carbon monoxide and carbon dioxide formation where as such products are normally formed at temperatures higher than 500°C for pure PVC[33]. Mostly the MBO's are chelate complexes of transition metals having an organic legand which can cleave at an elevated temperature thereby releasing the metal in a reactive state for it's action as FRSS. Dioctylpentadienyl iron (Ferrocene) was the first MBO which was widely acknowledged as a fire retardant smoke suppressant for PVC[31]. It increases char formation suggesting involvement in condensed phase. Other MBOs claimed effective in rigid as well as plasticised PVC are Vanadium ($\mathbb{II}$) acetylacetonate[25], Tris— (2, 4— Pentanediono) Chromum[51], zinc pyromellitate and iron pyromellitate[56]. While iron pyromellitate increases char yield by accelerating dehydrochlorination as well as rate of cross linking relative to fragmentation, zinc py-

romellitate meets only the first criteria but not the second (it accelerates both crosslinking and fragmentation[56]). The ability of iron pyromellitate to reduce fragmentation of PVC to organics including volatile and non volatile aromatic materials is relevant to smoke suppression. These additives limit the polyene length, thereby restricting intramolecular cyclization and promote formation of trans polyene sequence that cannot undergo intramolecular cyclization but that can crosslink.

Since the most effective smoke retarderts are precursors of oxidation catalyst[27]metal based organics must act as effective smoke suppressants.

6. 2 Fillers

Fillers are non polymeric compounding ingredients used at concentrations greater than about 20% of the polymer mass. They can be classified in to two arbitrary categories based on their apparent smoke suppressant functions: inert and active smoke suppressant filleres.

6. 2. 1 Inert Fillers

Inert Fillers can serve to reduce the amount of smoke generated from a given mass or volume of a polymer compound by diluting the amount of combustible substrate and by absorbing heat to reduce the mass burning rate; examples are: silica (SiO_2), asbestos, clay, barytes and carbon black.

6. 2. 2 Active Fillers

Active Fillers serve the same diluent and heat absorption functions as the inert fillers, but these absorb more heat per unit weight through endo thermal processes such as dehydration or calcination. The gases released during heating, such as water vapours, carbon monoxide and ammonia may also dilute the fuel mixture and intervene the flame process. Examples of active fillers include hydrates and carbonates, such as Aluminium Trihydrate ATH ($Al(OH)_3$)[57], Magnesium Hydroxide ($Mg(OH)_2$)[58], mangnesium carbonate, calcium carbonate[59]and microzeolite[60] etc. In all these the water of hydration and/or carbon dioxide is released at temperatures approximating those of polymer decomposition, producing both flame retardant and smoke suppressant effect. Molesky has presented FRSS mechanism of aluminum trioxide and magnesium hydroxide in a latest publication[61].

ATH undergoes endothermic dehydration over the temperature range 240—500℃ with the maximum rate of weight loss occuring at 250—300℃.

$$2 \ Al(OH)_3 \xrightarrow{\ 240-500℃\ } Al_2O_3 + 3H_2O + (+39) - (+72)Kcal. /mol$$
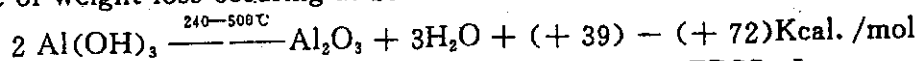
Because of these properties ATH has shown good effect as FRSS. It prevents the polymer from reaching the temperature at which significant breakdown; to yield combustible gaseous products; takes place[1]. Approximate decomposition temperature of magnesium hydroxide has been reported as 340℃[58].

$$Mg(OH)_2 \rightarrow MgO + H_2O$$
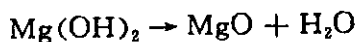
The mechanism of FRSS activity of $Mg(OH)_2$ in polymers is further disscussed by Hornsby and Watson[62]. ATH is found to be more effective in flaming conditions while magnesium derivatives eg. $Mg(CO_3)_2$ are more efective in smouldering conditions. The hydrates appear to function in condensed phase through their endothermicity, favouring cross linking reactions over the pyrolysis of the polymer. Flame retardancy and smoke suppression behaviour of $Mg(OH)_2$ and $Mg(CO_3)_2$ as functional fillers in flexible PVC formulations has been discussed by Levesque[63].

Calcium carbonate reacts with HCl released during combustion of PVC and absorbs HCl.

$$CaCo_3 \rightarrow CaO + CO_2 \qquad CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
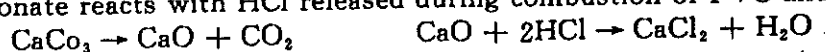
Microzeolite is available in native form having a general formula: Me $2/m$. Al_2O_3. n SiO_2. pH_2O(where Me=Fe^{+3}, Ca^{+2}, Mg^{+2}, Zn^{+2}, K^+, Na^+). They possess FRSS effects in PVC formulations when used in natural or modified form. The effect is best revealed by modified microzeolite containing 3. 5 to 4% zinc. Microzeolite and an organic additive such as amm. sulfamate combined with amm. sulfate act as a strong smoke suppressant additive in unplasticized PVC[60].

Use of fillers, in the quantities required to render the polymer FRSS, affects the physical

properties adversely, particularly the loss in tensile strength[2]. PVC—CaCO₃ composites have been found to have the elongation, yield strength, fractural strength and Izod impact strength reduced with the increase in filler contents[64].

6.3. Surface Treatment

The role of surface coating is one of insulation by removing the substrate polymer from involvement in combustion process and thus limiting its smoke contribution. A prime example is an intumescent paint, which chars and expands upon exposure to heat, forming a layer which insulates the polymer surface below.

6.4. Smoke Suppression in Plasticized PVC

The problem of smoke suppression in plasticized PVC is comparatively more complex. The introduction of plasticizer (eg DOP) increases the flammability of PVC. The plasticizer also contributes to the smoke generation fron PVC in a big way. The total amount of smoke from plasticizer and PVC is not additive but synergistic[18], probably because HCl (from PVC) accelerates the decomposition and changes the pyrolysis pattern of DOP.

The problem therefore consists of developing a PVC compound which has good flammability properties but produces little smoke ie FRSS. The two requirements are contrary to each other but can be achieved by using fire retardant plasticizer of phosphate type such as Tri cresyl phosphate (TCP). This results in good fire retardancy. However the phosphate type plasticizer may add to the smoke generation. The presence of phosphate inhibits the oxidation process. The amount of CO and CO₂ is slightly reduced. Additives are used to achieve the second objective of low smoke generation. Dioctyl azelate (DOZ) and ethyl hexyl oxalate have been reported as plasticizers for low smoke wire insulation[65, 66].

The additives normally effective in rigid PVC are also effective in plasticized PVC. Moore and Tsigdinos[34] have reported an effective formulation — 6 phr of MoO₃ causes decrease in smoke generation by 20%, 46% and 61% when the plasticizer (DOP) levels are 20phr, 60phr and 80phr. This indicates the effect of plasticizer on the efficiency of additives as smoke suppressant. Phosphate ester type plasticizers are used more for their fire proofing characteristics. These control the formation of phospheric acid and result in lowering the temperature of polymer accompanied by slight liberation of volatile products that decrease the flammability. Addition of 5 phr Sb₂O₃ to the system containing 100 parts PVC and 50 phr phosphate plasticizer has been reported to reduce smoke nearly by30%.

While in rigid PVC the role of smoke suppressant additive is in the solid phase — formation of char which is the residue obtained after dehydrochlorination of PVC, in plasticized PVC it is the modification of the pyrolysis mechanism and change in the products of decomposition of plasticizer[67].

7. Measurement of Smoke Evolved from Ploymers

A variety of laboratory test methods have been described for use in the measurement of smoke generation from polymeric materials[2, 68, 69]. They are generally based on either an optical measurement of light obscuration or on the gravitational filtration of soot particles.

The optical methods of smoke measurements are based on the application of Beer—Lambert Law which can be expressed as:

$$I_{(x)} = I_0 e^{-\sigma x}$$

where I_x = the light intensity attenuated by smoke layer
I_0 = the light intensity at source
σ = the attenuation co efficient
and x = the path length through smoke
or $\log_{10} I_0/I_{(x)} = x/2.303$

for a given path length, the expression on the left hand side of the above equation is proportional to smoke concentration, which is therefore a measure of smoke density and is termed as optical density of smoke 'D' expressed as:

$$D = \log I_0 / I_{(x)}$$

There is a correlation between the quantity of smoke determined by a gravimetric and the optical method[70]. The smoke measurement methods based on the optical method differ[71]in : (1) static and dynamic methods, (2) orientation of the light beam and the specimen and (3) source of the incident energy on the specimen. The main method utilizing the gravimetric apporach is Arapahoe Smoke Box (ASTM D 4100—1982) where the exhaust gases are sucked by vaccum through glass filter and weighed.

The important optical test methods are:

In static methods — — NBS Chamber(ASTM E 662, NFPA 258—T 34 and BS 6401), ISO Chamber (DIS 5924 ISO/TC 92) — smoke is accumulated in a closed box where it is measured.

In dynamic methods — — Steiner Tunnel test (ASTM E 84), OSU — RHR test (ASTM E 906), NBS Cone Calorimeter (ASTM E 1354) and Room Corridor test (ASTM E 603) — the smoke is measured as it escapes from the apparatus.

The most commonly used method — — NBS chamber — — is used to study the smoke generation in the flamming and non flamming modes. Smoke is measured by recording light transmittance as a function of time, however since Beer—Lambert Law is applicable only for mono chromatic light[72]the white light source is being replaced by He—Ne laser beam[73]. Sharma et al[74] have reported a method for smoke measurement in flow system using He—Ne laser which is reported to be particularly applicabel to the study of effectiveness of smoke suppressants in polymers.

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