Polyvinyl chloride, briefly termed as PVC, is inherently flame retardant due to the presence of large amount (56.8%) of chlorine in its structure. When brought in contact with flame it decomposes with evolution of hydrogen chloride gas which is not flammable and hence does not support the process of burning and consequently fire extinguishes as soon as source of flame is removed. However, when used in combination with flammable plasticizers, for flexible applications, its chlorine content is reduced. When chlorine content of PVC compositions falls to about 32% it becomes flammable.

Plasticised PVC compositions containing substantial amounts of plasticizers are not only flammable but also produce noxious fumes and dense smoke when burnt. Smoke generation makes visibility poor, causes irritation to eyes and suffocation in breathing. Further in the event of fire in the multistoreyed buildings, the poor visibility created by dense smoke makes escape of imperilled persons difficult.

To overcome the problem of flammability of plasticised PVC compositions a variety of flame retardants have been reported. However, it is common phenomenon
that these additives adversely affect some other desirable property of PVC compositions. For instance, phosphate esters and chlorinated paraffin wax though synergistically improve flame retardancy of PVC compositions but reduce their thermal stability. Similarly antimony trioxide, which is widely used as flame retardant, turns the PVC compositions opaque.

Keeping in view the limitations of above referred flame retardants a detailed literature survey was carried out which indicated suitability of a few organoantimony compounds, as flame retardants, for transparent polymers such as unsaturated polyesters, polystyrene and epoxides. Taking cue from these studies it was decided to evaluate few thermally stable and safe to handle, organoantimony compounds as flame retardants in transparent plasticised PVC compositions.

For the purpose of evaluation as flame retardant and smoke suppressant, following compounds were synthesised.

i) Triphenyl antimony
ii) Triphenyl antimony dichloride
iii) Triphenyl antimony dibromide
iv) Triphenyl antimony dibenzoate
v) Triphenyl antimony dihydroxide
vi) Triphenyl antimony oxide
vii) Triphenyl antimony diacetate
viii) Tri-p-tolyl antimony
ix) Tri-p-tolyl antimony dichloride
x) Tri-p-tolyl antimony dibromide
xi) Tri-p-tolyl antimony dibenzoate
xii) Tri-p-tolyl antimony dihydroxide
xiii) Tri-p-tolyl antimony oxide.

For the synthesis of these compounds primarily Grignard and Fittig processes were used. However, reported methods of synthesis were modified to obtain improved yields. Compounds were purified by crystallization and were characterised by infrared (IR) spectroscopy, differential scanning Calorimeter (DSC) and thermogravimetric analysis (TGA).

By using dynamic TGA technique, initial decomposition temperature (IDT), initial procedural decomposition temperature (IPDT) and activation energy (E) were
determined for all the organoantimony compounds of this study. The primary thermograms of the compounds were also used to determine their maximum decomposition temperature (Ts) and thermal decomposition (TD) temperatures at different stages of weight loss.

After characterization organoantimony compounds were used to prepare plasticised PVC compositions with the help of a ribbon blender and two-roll mill and finally the compositions were converted into sheets of 150 mm x 150 mm x 3 mm by compression moulding. In all more than 75 compositions were prepared.

PVC compositions were evaluated mainly for their limiting oxygen index (LOI), smoke density, hydrochloric acid liberation, transparency and thermal stability. Volume resistance (V.R.), tensile strength (T.S.), and elongation at break were also determined for most of the PVC compositions. For arriving at definite conclusion, performance of organoantimony compound containing PVC compositions were compared with the performance of compositions containing antimony trioxide and those without any antimony compound.

It was observed that PVC composition containing 75 phr (parts per hundred parts of resin) of DOP,
1.5 phr of thermal stabilizer and 0.5 phr of lubricant had LOI of 20.5 and chlorine content of 32% which means that this composition will burn with a candle like flame in the mixture of oxygen and nitrogen gases containing 20.5% of oxygen by volume. This recipe was used as base material for preparation of PVC compositions of antimony compounds as it is also expected to burn in air having oxygen concentration of approximately the same order.

Though many of the organoantimony compounds had shown promise as flame retardants and smoke suppressants but triphenyl antimony and triphenyl antimony dichloride excelled. The most remarkable features of these compounds is that transparency of their compositions was as good as that of 3 mm thick sheet glass, a common glazing material.

When PVC is burnt nature of its decomposition products depends on many factors such as temperature of pyrolysis, atmosphere and composition of PVC formulation etc. etc. CO, CO₂ and HCl are the main decomposition products when PVC is pyrolysed in air at high temperatures (600°C and above). Thus to determine mechanism of
action of organoantimony compounds in imparting flame retardancy to PVC compositions, concentration of CO, CO₂ and HCl was determined in their decomposition products and results were compared with the values obtained for PVC composition without antimony compounds and those containing antimony trioxide.

It has been established that though CO, CO₂ and HCl are the main decomposition products of PVC compositions containing organoantimony compounds, their quantity and ratio is greatly affected by the nature and concentration of these compounds. Amount of CO and CO₂ is substantially increased when antimony trioxide in a PVC composition is replaced by an equal amount of organoantimony compounds. This happens because aromatic groups attached to antimony are also oxidatively pyrolysed to form CO and CO₂.

Smoke, particulate matter, and ash which are important decomposition products of PVC, have not been given due consideration in mechanistic studies of this nature. Attempt has been made in this work for the first time, to quantify smoke and particulate matter as hitherto they have been determined in terms of smoke density or optical density methods. These methods give only relative values and therefore are of limited
significance in the present context. For the measurement of smoke and particulate matter a special arrangement was made.

Mechanism of action of antimony compounds has been explained and it has been conclusively proved that during combustion, antimony is converted in-situ into volatile antimony trichloride which is an effective flame retardant. Results show that composition of combustion products i.e. CO, CO₂, HCl, smoke and ash is dependent on the amount antimony metal present in the PVC.

When PVC burns dehydrochlorination and chain scission start almost simultaneously. Due to chain scission secondary reactions follow in which hydrocarbons and other fuel products diffuse through the primary char layer, come in contact with oxygen at the surface, where they burn and get oxidised.

As the organoantimony compounds are more volatile materials they provide better flame retardancy as compared to antimony trioxide if amount of antimony contained in them is considered as a basis. Results also show that whole of antimony present in PVC compositions does not volatilise but only fraction of it does so.