

Technology Development for Flame - Retardant Low - Smoke Material for Wire and Cables for Sheathing Applications

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An attempt was made to develop technology for low-smoke flame-retardant cable and compound with elimination of toxic chemicals in the formulation. The extrusion trials using twin screw extruder and cable coating with single screw extruder were successful. Results of the evaluation of the cable and compound suggest that the composition seems to be satisfactory. However, large-scale production could not be taken due to the actual techno-economic viability of the commercialization. This study paved the way for DSIR-sponsored project for commercial exploitation under PATSER scheme.

Keywords: *PVC resin, Stabilizer, Plasticizer, Single screw extruder, Flame-Retardant Low-Smoke (FRLS), Compounding.*

1.0 INTRODUCTION

Polymer-based materials are used in every branch of industry, and their usage is based on rapid progress made in many of the polymers. Most of the polymer-based materials are combustible, release toxic and noxious gases during combustion. In view of these, lots of research is being carried out for in-depth study of the behavior of polymeric materials exposed to fire. The risk involved and the damage caused by fire, where polymers are present, are significantly high considering the modern methods of construction, erection of high rise buildings, thermal power plants, oil refineries and modern means of transportation. In all major fire accidents, dense smoke is formed during burning of materials, which leads to poor visibility, causing lot of problems for fire-fighting personnel, like difficulty in speedy evacuation from the fire zone under critical conditions. In order to counter this problem, many research and industrial laboratories are making attempts to render these materials fireproof and reduce smoke generation by adding suitable compounds or by changing the structure of the polymer itself.

The additives must have a minimum impact on physical properties and product cost.

The industrial growth has resulted in large amount of power generation, and expansion of power and distribution networks. Electric cables are designed to carry power and communication leads for long distances, can act as pathway along which fire can travel and spread. The causes for fire could be due to electrical malfunction, faults, arcing, lightning, switching surges, overloading, heating of conductor joints, single phasing, inadequate ventilation, etc. Fire involving these cables may cause the loss of life, as well as damage to the facilities and equipment. In order to avoid such disasters, there is an increased demand for improved flame-retardant cables and to reduce not only flame propagation but also smoke and toxic emission. The flammable characteristics of polymeric materials used in cable insulation and jacketing have been of great importance to the electrical industry over the years. Electric cables rarely cause fires but may assist the spread of flames and may produce smoke and toxic fumes when exposed to fire already in progress.

During the early part of the development period, the emphasis was on flame-retardant and to reduce flame propagation of cables. More recently, interest has centered in cables which evolve reduced levels of smoke and toxic fumes.

Polyvinylchloride (PVC) is being used abundantly for insulation and sheathing of electric cables. In case of a fire, normal PVC cables burn with difficulty, but in certain conditions; for example, when cables are installed vertically, PVC will burn and can cause fire to spread rapidly. Polyvinyl chloride is inherently flame-retardant and hence its compositions represent one of the largest markets for flame-retardant applications. In unplasticized form, PVC is flame-retardant due to its high chlorine content (approximately 57%). When PVC is compounded with diatomic ester plasticizers and other modifiers, the resultant compositions will usually be combustible. One kilogram of soft PVC when subjected to fire will emit 360 g of HCl gas, which when dissolved in water results in 1L of concentrated smoking hydrochloric acid. The flammability of plasticized PVC can be controlled by the use of suitable additives. In order to impart flame-retardance with low-smoke characteristics, and to minimize toxic gas formation during burning of PVC compound, additives involving elements like chlorine, phosphorus, antimony, alloys, inorganic compounds, coordination as well as several organometallic compounds are used. Low-melting sulphate glass has also been identified as an effective fire-and smoke-retarding additive for PVC [1].

1.1 History of the Flame-Retardant Chemicals Industry

Fire causes a huge amount of human suffering, as well as personal and business financial loss. For nearly a century, with mixed success, attempts have been made to remove the fire hazard from items encountered in everyday life. Man-made materials, in particular, have been the subject of intense research concerning their behavior in fires. Initial applications were aimed at reducing the combustibility of fabrics or substrates by coating them with chemicals. Later, the industry began to increase the fire-resistance of materials by incorporating an additive or reactive compound.

More recently, in what has developed into the largest market for flame-retardant chemicals, flame-retardancy is engineered into polymers and, thus, is a result of the inherent properties of the materials.

The market for flame-retardant PVC compounds is growing, as these plastics compete for increasing applications in residential buildings, industrial buildings, public buildings, automobiles, aircraft, upholstery and clothing. Other significant markets include electrical insulation and military equipment. The requirements for flame-retardancy are becoming more rigorous as these markets are penetrated, test methods have become more realistic and sophisticated and awareness of the inherent danger in using flammable materials is increasing. This awareness has been accentuated by the total destruction, by fire, of buildings that were supposedly fire proof due to combustible contents, furnishings and decorations.

1.2 Development/Design Criteria for Flame-Retardant Power Cables

In the event of a fire involving cable runs, the protective cable sheath of a multicore cable will be the first component exposed to the flames/or to the radiant heat flux. Thus, the design criteria for the development of cable sheath or jacket in fire must consider in optimizing the fire/pyrolysis behavior of materials. In general, it can be said that the task of the polymer expert is to develop new materials which are transformed from 'Easy to Burn' stage to 'Difficult to Burn' stage. New materials should also perform well in reducing the smoke generation and acid generation significantly. In addition, the cable insulating and sheath materials should have high fire resistance and maintain electrical integrity under conditions of electrical stress and exposure to flame so that essential services are maintained.

1.3 Fundamental Aspects of Burning of Polymers

Polymeric materials (hard or soft) are linear or cross-linked macromolecular organic materials which do not burn easily. However, their flammability arises from the fact that they are unstable at temperatures

of $\geq 200^{\circ}\text{C}$, providing a range of small volatile organic compounds, which are highly flammable. These products of thermal degradation evolving large amounts of heat cause further degradation, rapidly leading to serious fire. Most polymers decompose at temperatures between 220 and 500°C and rapid oxidation may start at approx. 150°C . The presence of oxygen plays a main role in the decomposition as long as the surface is not flaming. This is because the oxygen depletion in the actual flame is so large that little amount of oxygen is enough to reach the burning surface. The decomposition is then almost a thermal decomposition. Once this situation is reached, it is said that fire has developed and combustion is in progress.

1.4 Theory of Processing of PVC with Additives

The normally used processing additives for PVC are plasticizers, stabilizers, lubricants, fillers, etc.

1.4.1 Plasticization of PVC

PVC is unique in its acceptance of large amounts of plasticizers with a gradual change in physical properties from rigid solid to soft gel or viscous liquid.

Method of Plasticization: The plasticizer is incorporated into the PVC resin by means of hot compounding. This process requires an energy input by heating, accompanied by vigorous mixing. At laboratory scale, the plasticizer and resin powder are mixed in a plasticorder at $150\text{--}170^{\circ}\text{C}$. The resin-plasticizer blend initially offers very little resistance to mixing. A slight increase may be noticed as dry blending takes place. As the resin-plasticizer blend begins to fuse and plasticization occurs on the surface, resistance to mixing increases rapidly. This is seen by the sudden increase in torque in the plasticorder. Some of the commonly used plasticizers are phthalates, phosphates, paraffinic oils, naphthenic oils, etc.

1.4.2 Stabilization of PVC

At processing temperatures used in practice ($150\text{--}200^{\circ}\text{C}$), sufficient degradation may take

place during the standard processing operations to render the product useless. Under the effect of heat and light/UV radiation, polyvinyl chloride loses its HCl molecule continuously, soon leading to a chain segment of polyunsaturation, resulting in the loss of mechanical or electrical properties. To eliminate this effect, certain materials known as stabilizers must be added. It has been found that incorporation of stabilizers retards or moderates the degradation reaction so that useful processable materials may be obtained.

There is a great deal of uncertainty in the mechanism of PVC degradation, but certain facts have emerged. Firstly, dehydrochlorination occurs at an early stage in the degradation process. There is some infrared evidence that as hydrogen chloride is removed, polyene structures are formed. At one time, it was thought that the liberated HCl caused autocatalytic liberation of further hydrogen chloride, but there is now growing evidence that this is not the case.

A second fact that has emerged is that oxygen has an effect on the reaction. It is believed that oxygen can cause both chain scission and cross-linking reaction, while it has also been observed that the presence of oxygen accelerates color formation.

The first physical manifestation of degradation used in the widest sense is a change in the color of PVC. Initially, on heating, water white will turn, in sequence, pale yellow, orange, brown and black. Further degradation causes adverse changes in mechanical and electrical properties.

The choice of a stabilizer, thus, becomes an empirical yet systematic process. The following factors are the most important that must be considered.

1. The grade of the polymer used.
2. The nature of other ingredients present.
3. The cost of stabilizer required to give adequate stabilization for the processing and anticipated service life of the compound.
4. The clarity of the compound required.
5. Toxicity.

6. The effect on lubrication, printing, heat sealing and plate-out.

The most important class of stabilizers are the lead compounds, which form lead chloride on reaction with hydrogen chloride evolved during decomposition. They are also good heat stabilizers. Of these materials, basic lead carbonate ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) has been, and probably still is, the most important stabilizer for PVC, on which it confers excellent thermal stability and electrical resistivity at temperatures around 160°C . It may be considered as typical of the lead compounds and has a low weight cost. One disadvantage of lead carbonate is that it may decompose with the evolution of carbon dioxide and water at the higher range of processing conditions of above 190°C , thus leading to a porous product.

For this reason, at higher working temperatures, tribasic lead sulphate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$) has been found to be a good heat stabilizer. It is in itself very stable to heat and can be heated without decomposition to temperatures well in excess of those normally encountered in compounding and fabricating PVC, such as high speed extrusion. In the absence of any decomposition, it ensures sound products with complete absence of porosity caused by evolution of gases. It gives polymer compounds better electrical insulation property than lead carbonate. Its weight cost is somewhat higher than that of lead carbonate, but less than most other stabilizers.

1.4.3 Addition of Fillers

Fillers are commonly employed in opaque PVC compounds in order to reduce the cost. They may also be employed for technical reasons such as to increase the hardness of a flooring compound, reduce tackiness of highly plasticized compounds, improve electrical insulation properties and improve the heat deformation resistance of cables.

In evaluating the economics of a filler, it is important to consider the volume of filler that can be added before bringing the processing and service properties below that which can be tolerated. Thus, in some cases, it may be more economical to use

a filler with a higher volume cost because more can be incorporated. To judge the economics of a filler simply on its price per unit weight is of little merit. For electrical insulation, China clay is commonly employed, whilst magnesium carbonate and various calcium carbonates are used for general-purpose work.

1.4.4 Addition of Lubricants

In plasticized PVC, the main function of a lubricant is to prevent sticking of the compound to surfaces of the processing equipment working at high temperature and speeds. This is brought about by selecting a material of limited compatibility which will thus sweat out during processing to form a film between the bulk of the compound and the metal surfaces of the processing equipment. Calcium stearate ($(\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2)$) has been used most commonly with non-transparent products, and stearic acid with those that are transparent.

1.4.5 Means of Imparting Flame Resistance to PVC

Most commercial plastics burn fairly easily even under moderate conditions. Therefore, it is a common practice to use flame-retardants (FRs) for improving the fire-resistance performance and reducing the tendency for smoke emission. Today, a variety of different FRs are available in the market which are often tailor-made for specific applications. FRs are compounds that possess special structural or chemical features that can modify and transform the properties of polymers in such a way that they retard the flame and emit low smoke. Elements such as phosphorus, halogens, etc. are used to transform polymers to FRs which not only give high performance, but are also cost-effective.

The most common approach that is adopted by the industries for flame-retardance is the use of halogenated flame-retardants. Halogen can be added to the system as flame-retardant, but are more efficient when incorporated into the substrate of the polymer as a reactive flame-retardant. However, these retardants develop thick smoke and corrosive gases. The polymers

with high amount of inorganic fillers are suitable for reducing smoke.

The design of flame resistance into plastics is essentially based on empirically gained knowledge. The role of active smoke-retarders is to change the thermal degradation pattern of PVC and to promote the formation of char. In practical form (i.e. taking into account economic limitations and performance characteristics), flame resistance is imparted by the incorporation of halogen-bearing compounds, specifically chlorine and bromine, phosphorus-or boron-containing compounds, and by nitrogenous materials, either singly or used in combination. Their effectiveness can be, and frequently is, augmented by auxiliary synergistically acting compounds. Flame-retardants can be classified into three categories:

- (a) **Reactive type** : The fire-retardant reacts chemically with the polymer components and is combined chemically into the basic polymeric structure.
- (b) **Additive type** : The fire-retardant is physically blended into the base polymer prior to conversion to the final product. These types are usually preferred for thermoplastic polymers.
- (c) **Co-additive type** : This includes compounds which by themselves are ineffective as flame-retardants, but in the presence of halogen, phosphorus, nitrogen or boron-containing compounds provides synergistically improved flammable characteristics.

1.5 Metal-Based Flame-Retardants

For many years, metal hydroxides have been established to substitute critical organic FR in applications where the human life is directly threatened in a fire. The halogen-and acid-free character of such substances in combination with halogen-free plastics is promoting and pushing the trend to use environmentally benign products. During combustion, metal hydroxides do not evolve toxic or corrosive gases as well as remarkably suppress the emission of smoke.

Nowadays, the most widely used acid-free and halogen-free flame-retardant is aluminium

trihydrate (ATH). ATH acts as a mineral flame-retardant and smoke suppressant because of its thermodynamic properties. $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ contains 34.6% of water. The retardant is obviously effective because of the heat required to decompose the hydrate and evaporate the water. When exposed to heat, it will absorb about 280 cal/gm before liberating water vapor. At 200°C, chemically combined water of hydration begins to liberate. This endothermic decomposition absorbs thermal reactive energy from the flame. The endothermic cooling is believed to favor dehydrogenation reactions and protect char formation. The evolution of water not only has a cooling effect but also blankets the flame and acts as a diluent. The aluminum oxide layer, formed by dehydration, has an exceptionally high surface area. The high surface area of alumina absorbs smoke and flammable molecules, causing a reduction in the amount of carbon dioxide evolved. It has been suggested that ATH acts as an electron donor to terminate radical reactions, by giving rise to relatively unreactive inorganic free radical, which is incapable of initiating further radical reactions. Other excellent properties include electrical arc/track and corrosion resistance.

1.5.1 Smoke Suppressants

Copper oxalate and ammonium molybdates provide an effective combination in PVC compositions to suppress smoke formation on fire without having adverse effects on the properties of the polymer composition. These additives are normally used in powder form in amounts of about 1–20 phr. These can be easily mixed with PVC in the powder form.

Smoke suppression by char formation can be achieved by using low-melting sulphate glasses. When heated, these systems form a cellular foamed char on the surface, which is thermally stable and protects the underlying polymer from the action of flames. Low-melting ternary sulphate and modified sulphate glasses based on transition metals like copper and nickel reduce the smoke generation during burning of the PVC compound.

The objective of this work was to develop the technology for flame-retardant low-smoke material for wires and cables for sheathing applications.

2.0 EXPERIMENTAL WORK

2.1 Blending/Compounding of PVC Formulations

PVC formulations were made by carefully examining the functions of the individual ingredients and their effect on physical, mechanical, thermal, flame-retardant and electrical properties of the compounded PVC product. Predetermined quantities of the PVC resin, stabilizer, plasticizer, filler, lubricant, antioxidant and flame-retardant additives with sulphate glass as a special additive were charged. Brabender Plasticorder PLE 331, which gives twin screw mixing action, was used for compounding the formulations at temperatures between 160 and 170°C. Known quantities of raw materials were mixed and were transferred into the Plasticorder and blended thoroughly for 5–10 minutes. The homogeneously compounded material was fabricated into sheet specimens (150 mm × 150 mm) using compression moulding machine maintained at 170°C under a pressure of 25 psi. The sheet specimens were used for evaluation of mechanical and flame-retardant properties. Different chemicals used in this study are listed in Table 1.

Chemical	Category
Polyvinyl chloride	Resin
Calcium zinc stabilizer	Stabilizer
Calcium carbonate	Filler
Tri-octyl-trimellitate, dioctyl phthalate, diisodecyl phthalate	Plasticizers
Bisphenol-A	Antioxidant
Calcium stearate	Processing aid
Antimony trioxide	Flame-Retardant additive
Ammonium molybdate	Flame-Retardant additive
Trihydrated alumina	Flame-Retardant additive
Low-melting sulphate glass	Flame-Retardant additive

The compound consists of common PVC filled with mineral flame-retardants and some other additives in minor amounts as indicated in Table 2.



FURNACE FOR GLASS MAKING

Component	phr
Resin	100
Stabilizer	4–7
Filler	10–30
Plasticizer	30–45
Processing aid	1
Flame-retardant additives	50–60
Sulphate glass	5–25

3.0 RESULTS AND DISCUSSION

PVC formulations, as described above, have been made and designated as C1, C2, etc. A large number of formulations have been studied with various plasticizers, stabilizers, fillers and flame-retardants additives, including sulphate glass.

The study also includes some of the commercially available raw materials like martinal, mica powder, etc. The compositions which have been selected for extrusion trials along with their properties are listed in Table 3. The flame-retardant properties of PVC compound with variation in sulphate glass (phr) are presented in Table 4.

The addition of low-melting sulphate glass to PVC composition while marginally increases

the oxygen index values, appreciably decreases the smoke density rating values [2,3]. As the concentration increases, thermal stability and to, certain extent, the percent elongation values decrease. This decrease in stability and elongation has been restored by the use of trioctyltrimellitate (TOTM) plasticizer in place of dioctyl phthalate (DOP) or diisodecyl phthalate (DIDP) plasticizers. The properties obtained from CPRI -developed formulations compared with different

Formulation	Oxygen index (%)	SDR (%)	TS (N/mm ²)	Elongation (%)
Required	29–30	50–55	12.5 (minimum)	150 (minimum)
1	29.0	51	14.88	162
2	31.5	46	13.82	141
3	29.3	56	13.65	171
4	29.9	56	13.76	172
5	30.6	43	13.48	126
6	31.3	56	14.11	156
7	29.0	55	13.15	145
8	31.1	55	15.20	137

Property	Reference compound	Low-melting sulphate glass (phr)		
		10	20	40
Oxygen index (%) (ASTM D 2863)	30.4	30.8	32.8	30.7
Smoke density rating (%) (ASTM D 2843)	65–70	56–64	48–52	47–50
Tensile strength (N/mm ²) (ASTM D 638)	12.5–14.0	13–15	14–16	14–17
Elongation in percentage (IS 1554, P-I)	150–175	150–160	140–150	120–135
Thermal stability (min) 200°C	100	85	80	65

specifications for FRLS product [4] are given in Tables 5 and 6.

Note:

- (1) The properties obtained are within the specified limits of BIS.
- (2) The thickness of the cable extruded appears to be less than the required value. This can be adjusted at the time of cable extrusion.

3.2 Highlights of the Achievements

- (i) Development of low-smoke flame-retardant Cables and Compounds.
- (ii) Attempt to eliminate the toxic chemicals in the formulation of the compound.
- (iii) Extrusion trials using twin screw extruder and cable coating with single screw extruder were successful.

Properties	Industry Spec.	BIS Spec.	CPRI Results	Aim
Oxygen Index (%)	30	29	29–34	31
Smoke density (%)	60	60	45–65	40–60
Tensile strength (N/mm ²)	12.5	12.5	10–17	12–14
Elongation (%)	150	150	100–180	>150
Thermal stability (min), 200°C	80	80	80–90	80–90
Acid generation (%)	≤20	≤20	≤20	≤20
Volume resistivity (Ω-cm)	1×10 ¹³	1×10 ¹³	1×10 ¹³	1×10 ¹³

Properties	Values obtained	Required values
Oxygen index (%)	30.5	Min 30
Smoke density (%)	56.8	<60
Tensile strength (N/mm ²)	13.6	Min 12.5
Elongation (%)	171	Min 150
Thermal stability (min), 200°C	85	>80
Acid gas generation (%)	14.7	20 % maximum
Shrinkage (%) (150°C for 15 min)	1.31	4.0 % maximum
Volume resistivity Ω-cm, RT × 10 ¹⁵ 70° C × 10 ¹⁰	1.03 3.04	1 × 10 ¹³ 1 × 10 ¹⁰
High voltage 3 kV, 5 min	withstood	To withstand
Insulation thickness (mm)	0.853	0.90 mm

3.2 Techno-economic Viability of the Commercialization of Results of the Project and Plans to Commercialize

Results of the evaluation of the cable and compound suggest that the composition seems to be satisfactory. However, as large-scale production was not possible, the actual techno-economic viability of the commercialization could not be done (costing).

3.3 Suggested Future Development Work

Based on the detailed study conducted both at laboratory and at an industry, the following suggestions/observations are offered:

- (i) The development of low-melting sulphate glass seems to be remarkable as far as reduction of smoke during combustion of the PVC compound is considered. The use of this raw material in addition to the other ingredients in the composition also supplements in the elimination of the toxicity in the system. However, there was no consistency in terms of the results obtained at different laboratories.
- (ii) This inconsistency in results has forced us to take up further study to ascertain the reason for this behavior.
- (iii) The study suggests that the processing of the compound at laboratory level by using plasticorder can give compression-free mixing and a specific polymer structure.
- (iv) Further detailed study was conducted at industry using twin screw extruder which is altogether different than the laboratory type of mixing, wherein the mixing is made at high compression which disintegrates the polymer into smaller fragments, and this probably may be responsible for different polymer structures/complexities which end up in giving inconsistent test results.
- (v) The detailed investigations carried out at the laboratory (CPRI) to develop halogen-free low-smoke compound using higher

amount of ATH suggests that the processing/compounding is by making use of kneader-type low-compression mixing [5].

4.0 CONCLUSIONS

- (a) Several formulations of PVC compounds have been established for FRLS applications.
- (b) Initial extrusion trials undertaken at local cable industry are satisfactory.
- (c) This study paved the way for DSIR-sponsored project for commercial exploitation under PATSER scheme.

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