

# **Chlorinated rubber for flame resistant elastomers**

**By**

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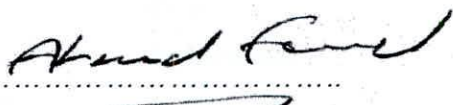


The work describe in this thesis was carried out by the undersign at London Metropolitan Polymer Center, London Metropolitan University, 166-220, Holloway Road, London. N7 8DB. United Kingdom under the supervision of Dr Ahmed S Farid & Dr Sudantha Liyanage, and a report on this has not been submitted to any university for another degree. Also, I certify that this thesis does not include, without acknowledgement, any material previously submitted for a Degree in any university and to best of my knowledge and belief it does not contain any material previously published, written or orally communicated by another person except where due reference is made in the text.



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## CHLORINATED RUBBERS AS FLAME RETARDANT ELASTOMERS

Elastomers with high chlorine content in their structure are more resistant to flame. There are variety of choice of elastomers type and grade that contain different level of chlorine concentrations. Traditionally, polychloroprene (CR) elastomers are used as flame resistant elastomers. Despite it has been used satisfactorily for a long time, modern application requires longer exposure to flame/heat or higher temperature increase the needs of better flame retardancy. Relevant industries such as transportation i.e. train, aeroplane, as well as petroleum rigs, civil engineering and even aerospace consistently revise their flame retardancy standards to improve safety. CR flame retardancy is limited to certain period of exposure and temperature. Apart from that, these applications often require excellent chemical and mechanical properties. These requirements occasionally exceed CR capability. Therefore it is expedient to investigate other elastomers with better engineering properties but at least comparable to CR in flame retardacy. Two elastomers have been identified as potential flame resistant elastomers. Chlorinated Polyethylene (CM) is chosen because of its low cost, better thermal resistance and will not degrade easily. Epichlorohydrin is recognised as potential flame retardant elastomer due to its chlorine content and broad range of service temperature.

Apart from mechanical properties, various test methods to study their flammability including *UL94* were also used. Limiting Oxygen Index (LOI) was also performed. The results were compared and discussed in this study. Chlorinated Polyethylene found to be the elastomer to replace polychloroprene. This found to have 36% of LOI test value and categorise as V 0 in UL 94 test.



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# Chapter 1

## INTRODUCTION

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Elastomers, like all organic substances are capable of burning. Much attention has been paid to the resistant of elastomers to flame. A lot of previous work has been done to investigate in improving the flame resistance of these materials.

Elastomers, which contain more chlorine in their structure, are more resistant to flame. Variety of elastomers has chlorine, in various concentrations. Traditionally, elastomers used to satisfy the flame resistant requirement is polychloroprene, although different grades will contain different amount of chlorine<sup>[1]</sup>. Despite the fact that it has been used satisfactorily for a long time, the modern application requires better flame resistance. Relevant industries such as transportation i.e. train, aeroplane, petroleum rigs, consistently revise their flame retardancy standards to improve safety. Apart from that, these applications require high engineering properties which occasionally exceed the polychloroprene capability. In addition to polychloroprene, two other elastomers have been identified as potential flame resistant rubber materials. Chlorinated Polyethylene (CM) is chosen because of its low cost, better thermal resistance and slow degradation. Epichlorohydrin also has a potential to be developed as a flame retardant elastomers due to its chlorine content and broad range of service temperature.

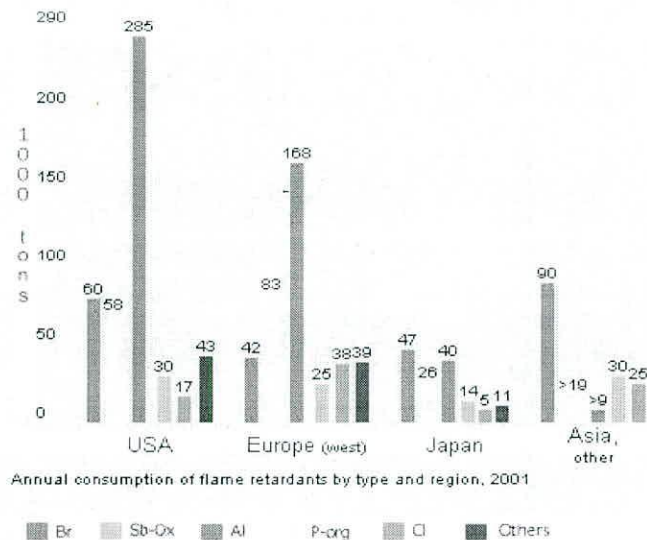
## 1.1 OVERVIEW

Fire is a serious issue around the world. Many countries through their relevant authorities are trying their best to reduce fire accidents. One way of doing it is by introducing flame resistant materials to be used in manufacturing consumer goods. This is particularly relevant to rubber and plastic materials which increasingly used as commodities<sup>[2]</sup> but can cause fire hazard.

Technological developments during the last century have led to the use of synthetic carbon based polymers for everyday house hold and office items i.e. furniture, fabric, automotive parts, where wood or metal might once have been used. The high fuel value of these materials means that their very presence could pose a danger, particularly in instances where a high risk of ignition is associated with the item's use. As a result the demands for the flame resistant materials grow rapidly in last two decades. After experienced various disasters related flammable materials, particularly in commercial transportation i.e. trains, planes, more and more country especially in Europe have subjected motor vehicles to legislative requirements for fire safety through the directive 95/28/EC. In England public transport vehicles are required to confirm to the standards lay out in BS6853 with title *Code of practice for fire precautions in the design and construction of passenger carrying trains*.

Improving the flame resistance of elastomers and maintaining the environmental safety in the same time is a challenge faced by material researchers. Most of the flame retardant elastomers contained halogens which will be released as toxic fumes when burn. German and Nordic national standards organisation have recently set the eco-labelling standards whereby equipment (such as house hold and office electronics housings) cannot be labelled as environmentally friendly if it contains certain chemicals including brominated flame retardants. Most of the flame retardants use in United States and Asia are based on Bromine as shown in figure 1.1





**Figure 1.1: Annual consumption of flame retardants by type and region, 2001.**

With regard to fire safety, in December 2004, CPSC (U.S. Consumer Product Safety Commission) has started the proceeding to set flammability standards for bedclothes. It begin with a notice in the Federal Register requesting public comments on the fire risks and possible approaches to reducing them. Bedclothes are the first item to ignite in about 80 percent of mattress and bedding fires and can contribute substantially to the risks associated with mattress/bedding fires. Same time According to the NFPA's National Fire Safety Survey findings: Although the U.S. has a higher fire death rate than Canada, Western Europe and the Pacific Rim, the majority of Americans are very confident about their fire safety. Older adults express the greatest confidence even though they have the greatest risk of fire death. Men are more confident about fire safety than women; although, of the two groups, men are at a higher risk of fire death. The majority of Americans feel safest from fire in their homes, when in truth, home fires account for roughly 80% of all fires - and they pose the greatest threat to life. The cost of operating public fire prevention services in the U.S. costs the taxpayers billions of dollars per year, most of which is spent on suppression of fire. Many people have the attitude that "fire only happens to other people." But until fire strikes their home and family, fire prevention is ignored. Once fire prevention week comes and goes each October, little thought is given to fire safety and prevention until next year's campaign. Fire suppression is a necessary and vitally important service. It is, however, "after-the-fact". This includes smoke detectors, alarms, sprinklers and extinguishers. The use of fire retardants or firestops are logical "before-the-fact" steps that should be taken. Fire spreads 1100% in the first 4 minutes. Heat rises at 90 feet per second or approximately 60 mph. Approximately



90% of fire fatalities are in the home and 90% of the fatalities occur during the sleeping hours 10pm to 6am. Remember, smoke alarms and sprinklers cannot prevent the fire, but fire retardants in most cases can prevent and/or slow the spread of fire, which can greatly prevent loss of life and property in addition to using smoke alarms or sprinklers.<sup>[3]</sup>

## 1.2 OBJECTIVES

**"Each year 600 people die in fires in Germany alone and 6000 are seriously injured".**

The Objective of work proposed to develop a new elastomer which is resistant to fire and the same time to achieve the given mechanical properties. Proposed vulcanite should pose the British Standard for flame retardancy. Polychloroprene compound was used to benchmark this research as it is traditionally and widely used as the flame retardant elastomer.

The objectives of the present work can be summarised as follows:

1. To formulate the flame resistant rubber compound using elastomer other than polychloroprene which can satisfy fire safety requirement according to ISO 9772, 9773 and ASTM D 2863 as outlined by *Vulcanite*, Australia.
2. To optimise the physical properties i.e. tensile strength, elongation and hardness of the flame retardant compound to suit its application.<sup>[4]</sup>

## 1.3 MATERIALS

### 1.3.1 Elastomers

Most of the elastomers which contain chlorine are more resistant to burn. With that basis, chlorinated elastomers are chosen for this research. Chlorinated Polyethylene (CM) and Epichlorohydrin (ECO) are used alongside the traditional flame resistant elastomer, Polychloroprene. They are all compounded based on typical flame resistant compound.

### a) Chlorinated Polyethylene (CM Tyrin CM3630E)

CM elastomer is polyethylene which contains various limits of chlorine in its back bone. CM grades differ mainly in the degree of chlorination (i.e. 25% and 42% by weight of chlorine), Mooney viscosity and amount of crystallinity. It is produced in solution, emulsion or in suspension polymerisation.

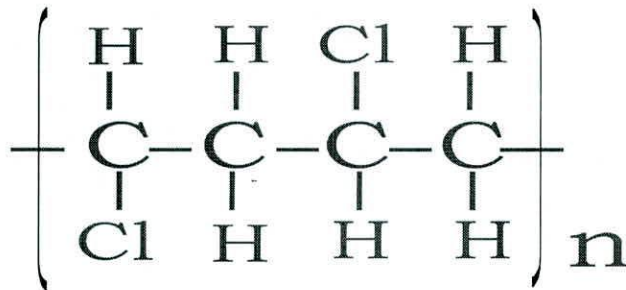


Figure 1.2 Structure of CM

Because of the lack of double bonds in CM, it has better resistance to chemical attack, improve weatherability, and heat. On the other hand it means that it is nearly impossible to establish crosslink by sulphur. Peroxide is the option and known as to gives good heat resistant to the compound. Like all other chlorine containing rubbers CM also have to be protected against HCl cleavage during vulcanisation by adding metal oxides to the compound. Suitable metal oxides are MgO and Lead Oxides. CM processing required strict temperature control. Normal vulcanising temperature is 150°C. Properties of vulcanisate are as follows:

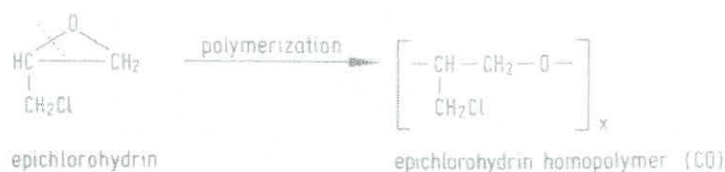
1. Good mechanical properties
2. Low compression set
3. Low brittleness temperature
4. Very good dynamic fatigue
5. Excellent aging
6. Better weathering and ozone resistant
7. Good oil resistant even in higher oil temperatures<sup>[5]</sup>.

Material data sheet of **Tyrim CM3630E** which was supplied by **Omya UK** <sup>[6]</sup>

Tyrim CM 3630E	
Aspect	Specification
Appearance	Powder
Colour	Light cream
Melting point range	80-120 C
Specifi gravity	1.3
Relative Density	1.1g/cm3
Water Solubility	Insoluble

### b) Epichlorohydrin (ECO).

Epichlorohydrin elastomers have higher chlorine content than do many other chlorine-containing elastomers. The homopolymer has the highest content of chlorine which out of all three derivatives. ECO formed by ring opening polymerisation of epichlorohydrin and ethylene oxide as shown in figure 1.1 & 1.2:



**Figure 1.3: Epichlorohydrin Homopolymer (CO)**



**Figure 1.4: Epichlorohydrin Copolymer (ECO)**

Hydrin H-55 elastomer used in the test is an epichlorohydrin homopolymer with high oil, fuel and solvent resistance. Supplied by Zeon Chemicals USA. Compounds using Hydrin H-55 typically exhibit good heat resistance, excellent ozone resistance along with outstanding gas impermeability. Sufficient antioxidant is added during the manufacturing process for normal aging conditions.

### c) Polychloroprene Rubber (CR).

Poly(2-Chloro-1,3-butadiene) or Polychloroprene elastomer was discovered in 1930 by W. H. Carothers and his co workers. Large scale production began in the USA in 1931/1932 by bulk polymerisation process. It was initially called as *Duprene* and later on it was become to known as *Neoprene*. At the beginning it was famous for high resistance for oil and excellent mechanical properties. Later on it has been used as flame resistance as well. CR is used in different technical areas, mainly in the rubber industry (61%) and also important as material or adhesives (33%). The typical delivery form of CR is 'chips' as it shown in figure 1.5:



Figure 1.5 CR Flacks.

Today CR is exclusively produced in emulsion, and using free radical initiators. With aid of radical initiators, polychloroprene in the foam of an aqueous emulsion is converted in to homopolymers, or in the presence of comonomers into copolymers as it shown in figure 1.4.

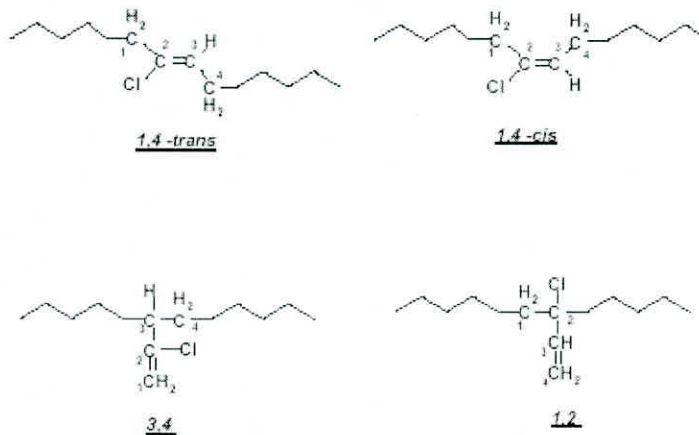
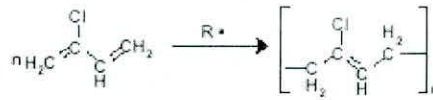


Figure 1.6: Polychloroprene

For this experimental work *Neoprene WRT* was used. Supplier was **DuPont Dow elastomers USA**.

Basic properties as follows:<sup>[7]</sup>

Neoprene WRT	
Aspect	Specification
Appearance	Chips
Colour	White to silvery gray
Odour	Mild, characteristic
Specific gravity at 25/4 C ASTM D7920-66	1.25
Mooney Viscosity, ML(1+4) at 100 C	41-51
Crystallization Rate	Very slow



## 1.4 CHEMICALS

### 1.4.1 Flame retardant

In this research work, the flame retardant additives used are:

- Antimony Oxide, supplied by **Omya UK** with the trade name of *Garoflame SB96DINP*
- Magnesium Hydroxide, supplied by **Omya UK** with the trade name of *Magnafin H5*
- Zinc Borate, Supplied by **Omya UK** with the trade name of *Zinborel®*

#### GAROFLAM SB96 DINP

Description	Antimony trioxide dust suppressed with di-isononyl phthalate		
Appearance	White non-dusting powder		
Plant	HUMBER, Great Britain		
Chemical analysis of the raw material	Sb <sub>2</sub> O <sub>3</sub>	≥	99.5 % *
	Pb	≤	0.1 % *
	As	≤	0.1 % *
Di-iso nonyl phthalate content	GB LTM 215		3.0 – 4.0 %
Antimony trioxide content	By difference		96 – 97 %
Sieve residue > 45 µm	GB LTM 016	≤	0.01 % *

\* Measured on untreated material

[8]

#### Magnesium Hydroxide & Aluminium Tri Hydrate.

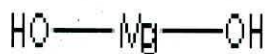


Figure 1.7 Magnesium Hydroxide

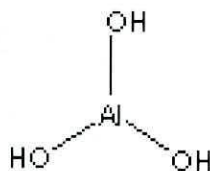


Figure 1.8 Aluminium Tri Hydrate

Aluminium Tri Hydrate (ATH) and Magnesium Hydroxide are the most important flame retardants in recent past. They function as flame retardant in both the condensed and vapour phase. When these additives are heated, it decomposes and release water that forms an envelope around the flame, which tends to exclude air and dilute the flammable gases. In addition this endothermic reaction lowering the ambient temperature. ATH ambient temperature is around 230 °C and magnesium hydroxide temperature is around 330 °C. But magnesium hydroxide forms char and produce less smoke than ATH. In general these compounds has very low levels of toxicity except when there are high exposure levels or unusual ways of exposure.<sup>[9]</sup>

### **Zinc Borate.( 2ZnO.3B<sub>2</sub>O<sub>3</sub>.3.5H<sub>2</sub>O)**

Zinc Borate is an important additive to help achieve excellent flame resistance in rubber articles. It is a free-flowing powder that disperses easily. Zinc borate can be added to any flame retardant system and will improve flame test results with minimal effect on compound properties. Zinc borate will form a glassy char at high temperatures that prevents flame propagation. It also releases water of hydration similar to ATH. Zinc borate is a synergist with antimony oxide and halogenated flame-retardants as well as ATH. The combined ingredients will have better flame resistance than the separate materials would have. Zinc borate helps in compounding halogen-free, flame-resistant rubber that generates minimum acidic smoke.

### **Antimony Trioxide. (Sb<sub>2</sub>O<sub>3</sub>)**

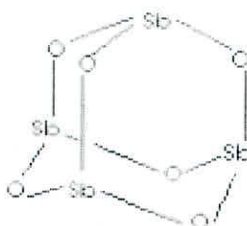


Figure 1.9 Antimony Trioxide

Antimony Oxide appears as white, polymorphic crystals. It is slightly soluble in water and soluble in most of the acids. It has a molecular weight of 291.52g/mol and has a melting point of 655C. Approximately around over 40000 metric tons will be using in US only per year. Major share of this used as flame retardant. Importantly, Antimony oxide has not been categorise as carcinogenic by USEPA.<sup>[10]</sup>

## 1.5 FILLERS

### 1.5.1 Kaolin Clay

Kaolin clay is the primary non-black filler in rubber, accounting for more than 50% of all non-black filler used. Of this, about 80% is air float hard clay, with calcined clay, delaminated clay and water-washed clay making up the balance. A review of kaolin clay and its performance in rubber compounds is best undertaken within the context of certain general considerations regarding the ways that fillers and elastomers interact. The characteristics which determine the properties filler will impart to a rubber compound are particle size, particle shape, surface area and surface activity. Surface activity relates to the compatibility of the filler with a specific elastomer and the ability of the elastomer to adhere to the filler. If the size of the filler particle greatly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Fillers with particle size greater than 10,000 nm (10  $\mu$ m) are therefore generally avoided because they can reduce performance rather than extend or reinforce. Fillers with particle sizes between 1,000 and 10,000 nm (1 to 10  $\mu$ m) are used primarily as diluents and usually have no significant affect, positive or negative, on rubber properties. Semi-reinforcing fillers range from 100 to 1000 nm (0.1 to 1  $\mu$ m). The truly reinforcing fillers, which range from 10 nm to 100 nm (0.01 to 0.1  $\mu$ m) significantly improve rubber properties<sup>[11]</sup>.

### 1.5.2 Carbon Black (FEF N 550)

Carbon black fillers are formed from pyrolysis of hydrocarbon materials whilst they are in vapour phase. The mechanism by which hydrocarbons can be thermally decomposed may be represented as follows:



Whatever the process by which hydrocarbons are decomposed the main requirement is to carry out the thermal decomposition in a limited supply of air. If hydrocarbons are in an abundance of air then combustion will take place:<sup>[12]</sup>

