BEHAVIOUR OF EXPANDABLE GRAPHITE AS A FLAME RETARDANT IN FLEXIBLE POLYURETHANE FOAM

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Abstract

"The growing trend of **substituting non-halogenated flame retardants** is sweeping the industry. Also along with this trend are the increasing demands upon the **improvement in the physical properties of the polymer.**

Expandable graphite plays a major role as a non-halogenated flame retardant in flexible polyurethane foam. This paper will address the **selection of flame retardant grades** of expandable graphite, which not only depends upon the **purity of graphite flake**, **particle size of flake** but also on the **expansion properties of expandable graphite** to expand at the temperature (critical temperature) where the polymer starts melting, decomposing and ignition begins.

This paper presents effects of expandable graphite and its contaminants on physical properties of flexible polyurethane foam".

Introduction

Internationally most countries are interested in establishing and sustaining high level of fire safety in consumer products. The role of flame retardants as a part of the solution is well recognized. Majority of the flame-retardants are still halogenated chemicals and they operate in the gas phase by diluting combustible gases. During flame retardant action, **there is a loss in the mass of the polymer**, which is very high and is **responsible** for producing **toxic gases** like carbon monoxide etc.. These gases are considered to be harmful and contaminate the fireplace and its surroundings due to its high toxicity.

Present need is to reduce the toxic gases during fire, this is possible by using non-halogenated flame retardant. However, non-halogenated flame-retardants also have some problem like high level of loading in to the polymer, which deteriorate the original properties of polymer. Although suitable solutions have not been found in all cases. However, it is possible in flexible polyurethane foam by the proper selection of expandable graphite as a non-halogenated flame retardant.

History

In 1964 it was first noticed that the solution for fire resistance is to make greater use of intumescent material which, when heated swells up and screens the combustible material from fire and oxygen.

In 1971 Frnaclxzek and co-workers, the Dow chemical invented the use of expandable graphite as a flame /fire resistance in various polymer which includes flexible polyurethane foam[1].

In 1976 it was also used for making flame retardant protective tube for electrical wires or cables.[2]

In 1981 Expandable / Exfoliated Graphite was commercially available for the extinction of metal fire[3].

In 1985 Bell, Dunlop used expandable graphite in synergetic combination with melamine to make flame retardant flexible polyurethane foam[4]. Fumio Okiskai Yokkaichi Research laboratory found limitation for the flame retardant performance of expandable graphite while using in the polymer[5].

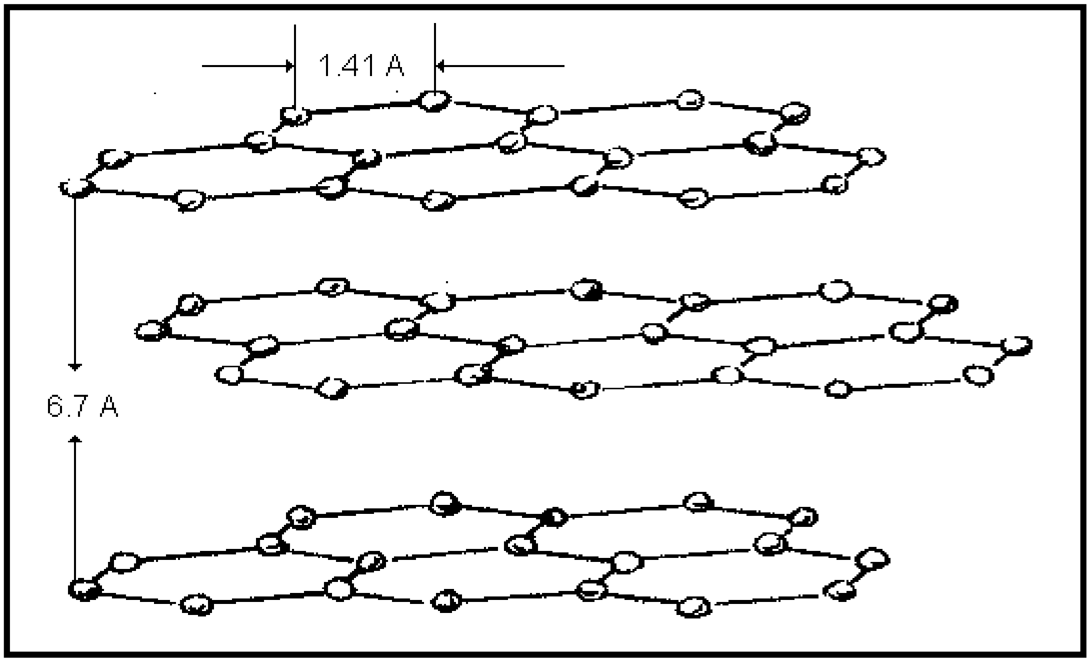
Our works demonstrate that limitation of flame retardant performance of expandable graphite can be overcome in the case of flexible polyurethane foam by the proper selection of expandable graphite and it is possible to minimize the deterioration of physical properties of polyurethane foam by using total expansion formula.

What is expandable graphite?

Expandable graphite is manufactured using natural graphite flake. Natural graphite flake is a layered crystals consisting of sheets of carbon atoms. The atoms are tightly bound to each other within a layer, but the layer themselves are weakly held together.

Expandable graphite is manufactured by the oxidation of graphite flake in sulphuric acid. The capillary structure of graphite flake permits them to absorb the acid readily. Intercalated graphite when heated at high temperature it swells/expands up about 100 times to its original volume. The origin of expansion lies in the vaporization of intercalates. The expanded/exfoliated graphite flakes are vermiform in appearance and have a circumference of ¼ inch –½ inch and length of sometimes several inches. The volume of these “worm” is often a hundred or more times than that of the original graphite[6].

Fig: 1



Crystal structure of Natural Graphite Flake.

Expansion rate increases as the flake size of the expandable graphite increases it also depends upon the intercalation stage i.e. amount of insertion compound in the layer of graphite[7]

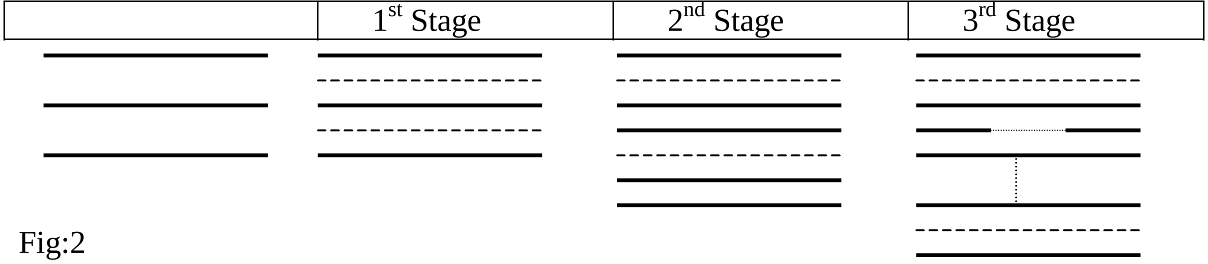
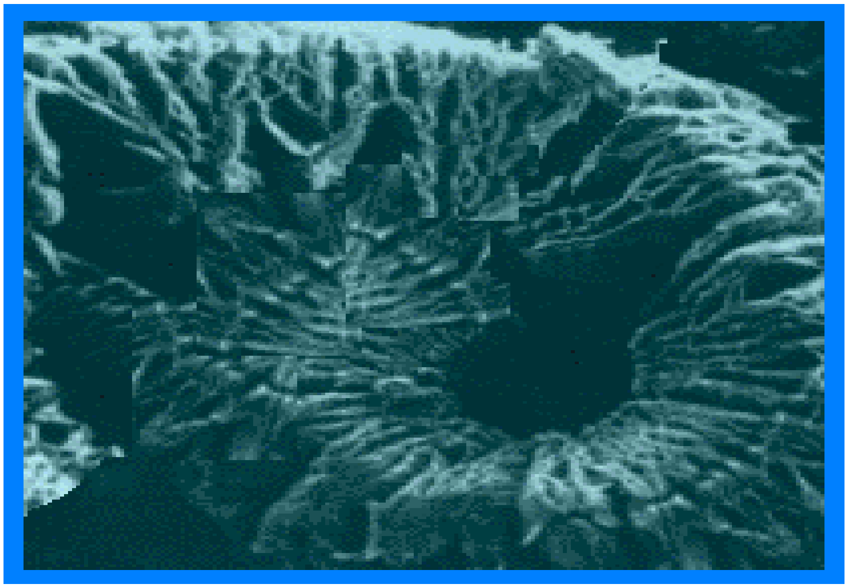


Fig:2

—— Graphite Layer .... Interlayer compound

How does expandable graphite work as a flame retardant?

Fig:3



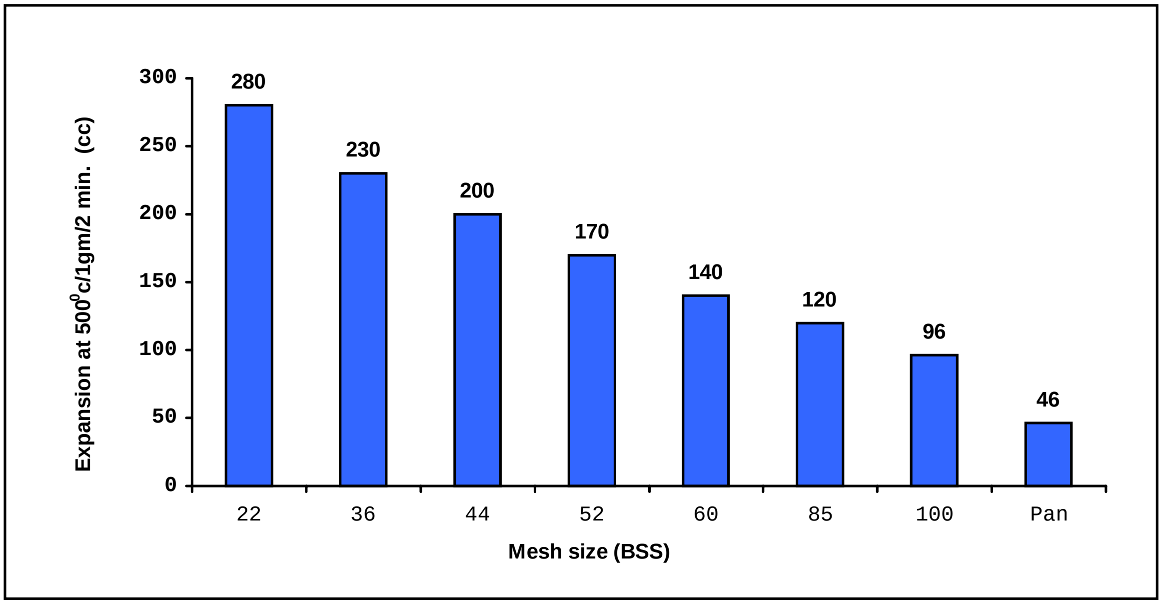
When expandable graphite is exposed to heat, it expands to more than 100 times its original volume and covers the entire burning surface by “worm” like structure of expanded graphite. Expanded graphite acts as a char former and also as an insulating agent due to the formation of small air gaps between the graphite layers[8]. It dramatically reduces the heat release, mass loss, smoke generation and toxic gas emission.

However, all expandable graphite does not act as flame-retardant, only low temperature expandable graphite act as flame retardant. The expansion must occur at “critical temperature” where decomposition, exothermal reaction and ignition occur spontaneously. This critical temperature range depends upon the chemical composition of polymer. Critical temperature in flexible polyurethane is 300^0C to 500^0C.

Observations of expandable graphite grades

1. Expansion of expandable graphite with respect to various particle size.

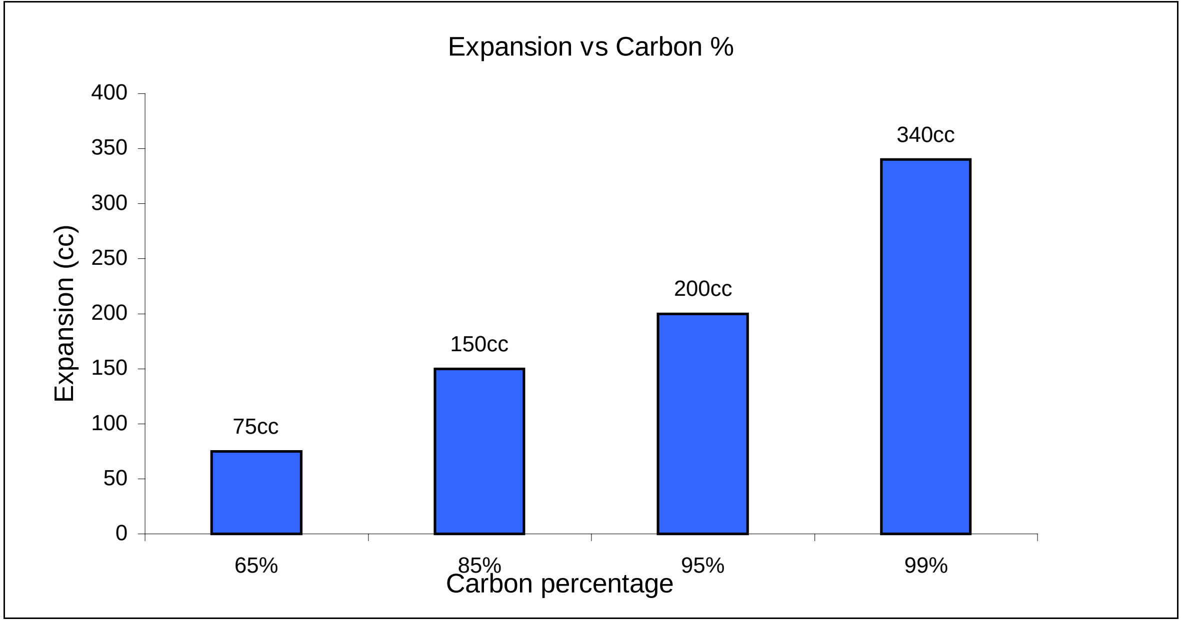
Graph: 1



The graph shows that expansion increases as particle size increases and vice versa.

2. Expansion of expandable graphite with respect to various carbon percentages.

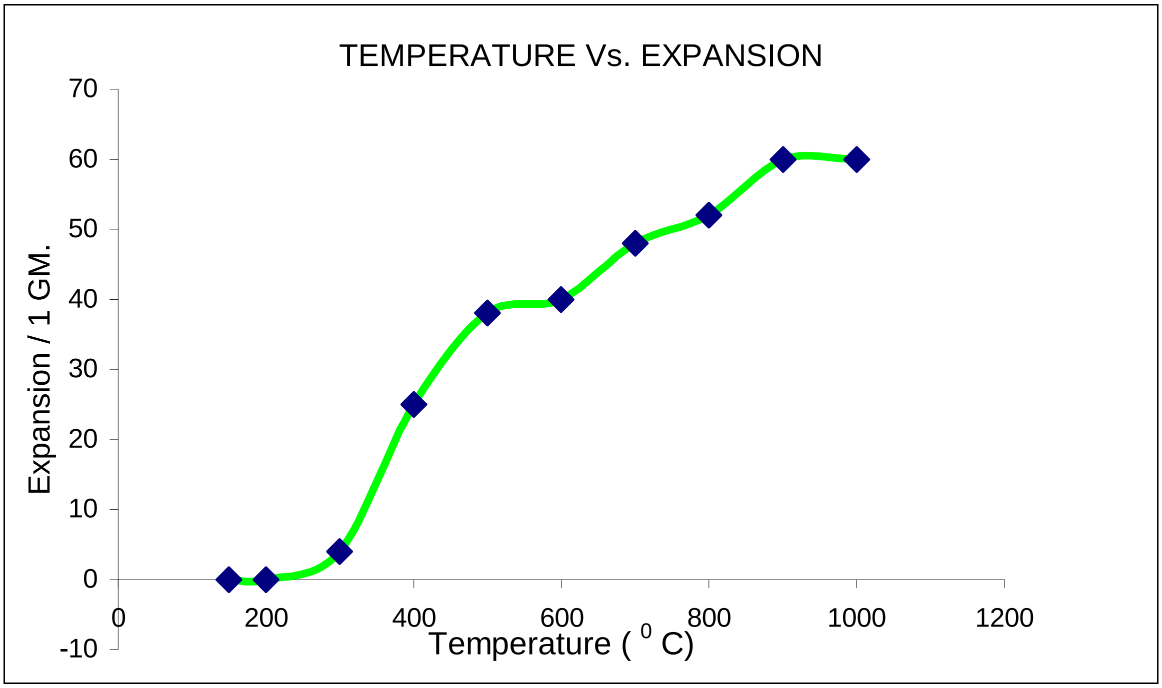
Graph:2



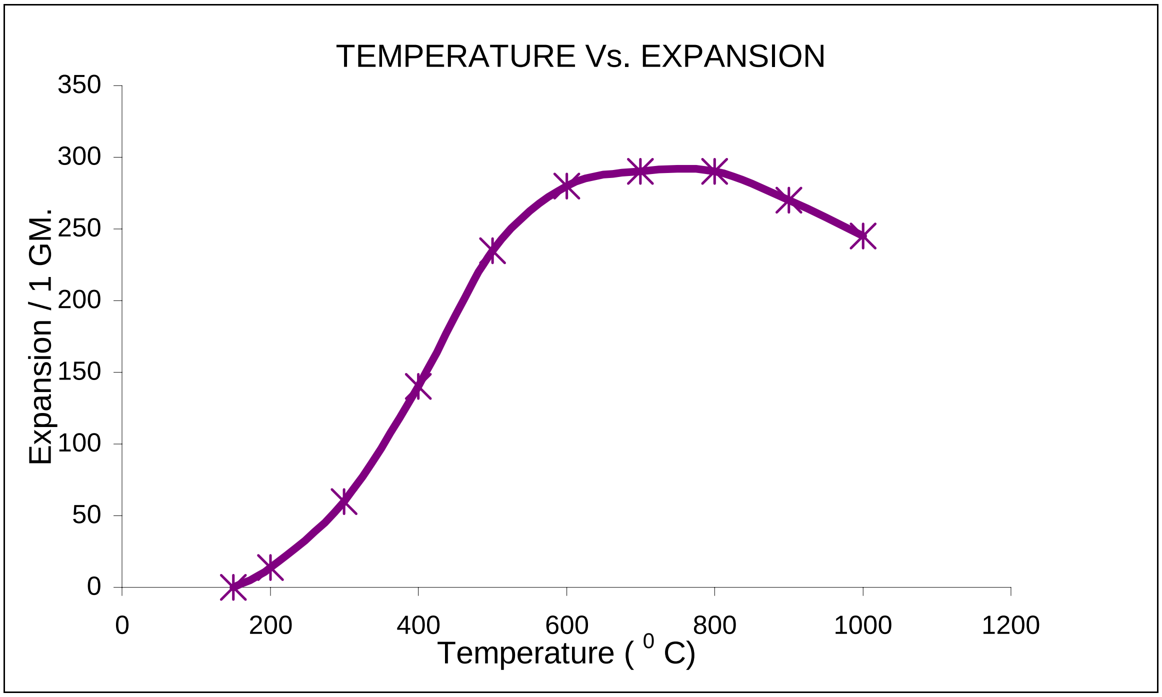
The graph shows that as the percentage of carbon increases the expansion rate increases.

3. Expansion properties of grade DW-20, PU-200 and LT-40

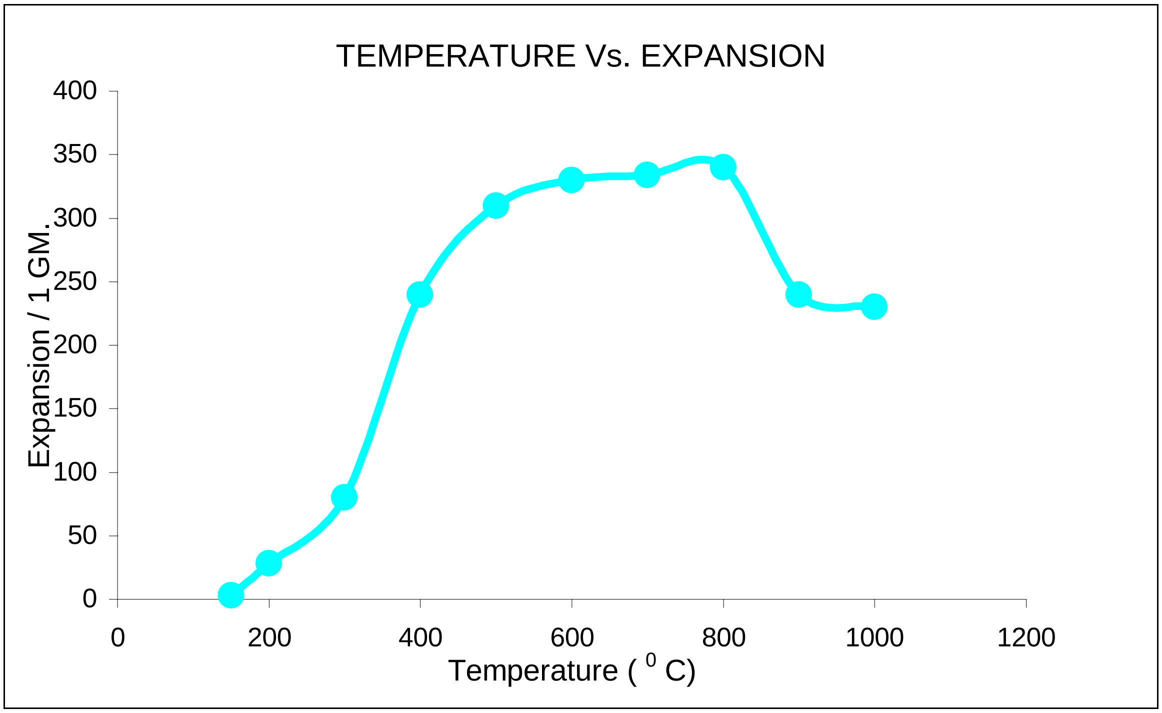
Graph: 3 (DW-20)



Graph : 4 (PU-200)

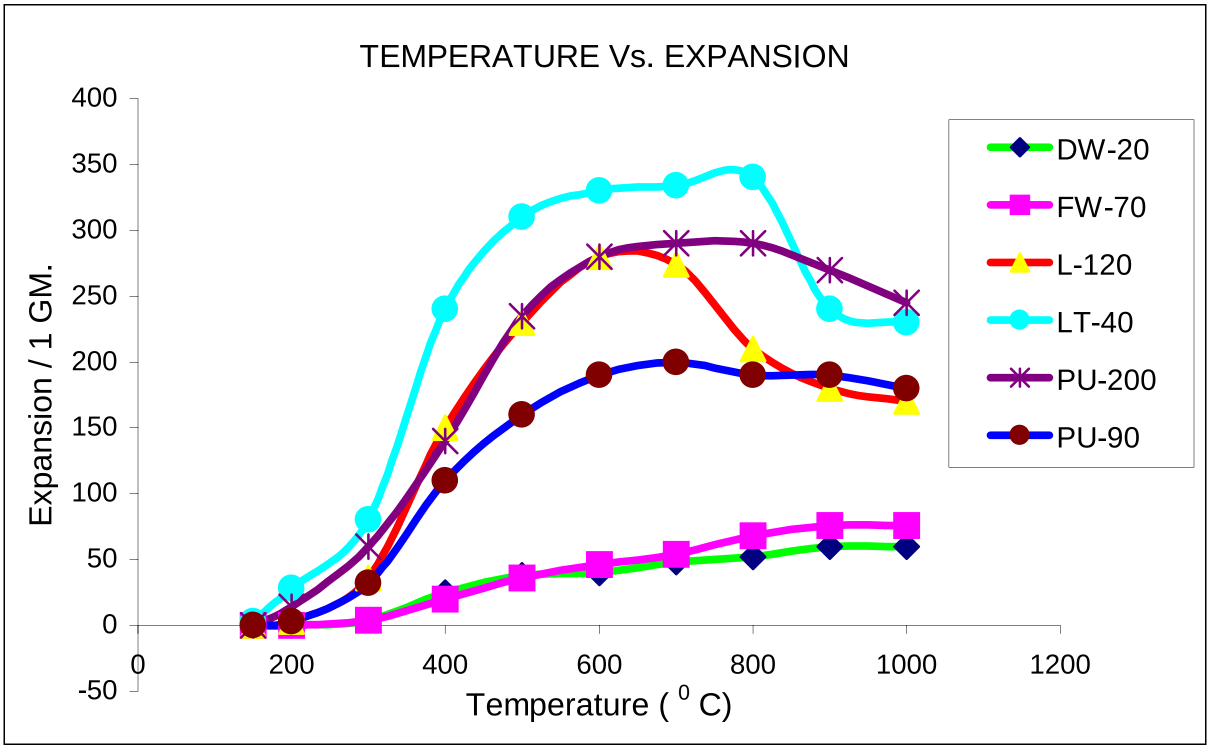


Graph :5 (LT-40)



4. Expansion properties of various expandable graphite grades.

Graph: 6



Experimental

Materials and methods:

The raw material used in the work were polyol (Avg mol wt 3500) T.D.I, stannous octate, Amine (DABCO), silicon polymer, water, & expandable graphite.

For the experiments we used the expandable graphite manufactured by Cleanline Products Private Limited, Pune, India[9].

Typical Analysis of Expandable Graphite

PROPERTIES	**GRADES**				
	110 LS	**PU-35**	**PU-90**	**PU-200**	**LT-40**
Expansion at 1000^{0}C	180 cc	110 cc	180 cc	260 cc	275 cc
Expansion at 500^{0}C	40 cc	38 cc	110 cc	220 cc	240 cc
Expansion at 300^{0}C	0	8 cc	32 cc	60 cc	80 cc
Expansion at 200^{0}C	0	0	3 cc	14 cc	28 cc
pH	07.13	07.25	07.07	07.12	07.18
Moisture	0%	0%	0%	0%	0%
Fe, Cu & Ni	Nil	Nil	Nil	Nil	Nil
Mesh (B.S.S.)					
+ 22 #	06 %	00 %	00 %	02 %	10 %
+ 36 #	46 %	22 %	22 %	38 %	58 %
+ 44 #	27 %	10 %	10 %	25 %	06 %
+ 52 #	04 %	12 %	12 %	12 %	05 %
+ 60 #	09 %	23 %	23 %	09 %	06%
+ 85 #	05 %	15 %	15 %	06 %	07 %
+ 100 #	03 %	09 %	09 %	02 %	08 %
+ 150 #		09 %	09 %	06 %	

Polyurethane foam formulation:

		[parts by wt.]
Polyol Average Mol. Wt. 3500	:	100.00
Expandable Graphite	:	35.00
Water	:	3.00
Silicon Polymer	:	1.20
Amine (DABCO)	:	1.20
Stannous Octate	:	0.23
Isocyanate (TDI)	:	48.66

Preparation:

The foam was prepared by hand mixing technique. Polyol is mixed with expandable graphite at 4000 rpm, then water, silicon polymer, Dabco(amine), Stannous octate are added with constant stirring, finally T.D.I. is added with constant stirring and poured into the cardboard box. Foam cured at room temperature for 24 hours (room temperature= 30°C) and then used for testing.

Test methods:

1) *BURNING PROPERTY* : Flame retardant properties were measured by flame torch method (Flame height - 2 ½ inch blue flame of Bunsen burner, 20 sec torching time, angle 45°) and oxygen index of expandable graphite is measured by standard method ISO-4589-1984(E).

2) *EXPANSION* : Dry the expandable graphite at 105^0C for one hour. Accurately weigh 0.75 gm, of the dried expandable graphite in to a dried, 100 cu-cm Nickel crucible and place in a furnace at 500^0C for 90sec and then allowed to cool in a desiccator. Pour expanded graphite in to dried measuring cylinder with out disturbing expanded crystals and measure the volume of the expanded graphite without tapping. Then calculate the expansion of 0.75 gm to 1 gm. $\frac{\text{Expansion}}{\text{Sample weight}}$ = Expansion per gram

3) *FIX CARBON:* is calculated by the following formula = [100 - (Ash + Volatile Matter)]

4) *ASH CONTENT* : Dry the expandable graphite for one hour at 105^0C, place 0.300 gm. of expandable graphite in a dried, pre-weighed crucible preferably platinum crucible. Place in furnace for 3 ½ Hrs. at 950^0C or until fully ash that is at constant weight. Re-weigh the remaining ash and calculate the ash content as a percentage of the original weight of expandable graphite.

$$\text{Ash Content (\%)} = \frac{\text{Loss in weight of sample (gms)}}{\text{Sample weight (gms)}} \times 100$$

5) *VOLATILE MATTER* : About 1gm sample before heat treatment is weighed by an analytical balance. It is then put in a Nickel crucible. The Nickel crucible is covered with a lid and place in electric furnace at $925^0\text{C} \pm 20^0\text{C}$ for 7 minutes. Then nickel crucible is cooled in the desiccator and is weighed by an analytical balance. The volatile matter is calculated with the help of the following formula.

$$\text{Volatile matter (\%)} = \frac{\text{Loss in weight of sample (gms)}}{\text{Sample weight (gms)}} \times 100$$

6) *DENSITY* : Expandable graphite is poured freely in to pre-weighed 10 cu-cm cylinder up to 10 cu-cm marking and then weigh the cylinder again & then calculate weight of expandable graphite. Density is calculated by following formula

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

7) *pH* : 10g.of Expandable graphite is added to 50cu.cm distilled water at room temperature. Stir well for 3 minutes and allow the expandable graphite to settle. Measure pH with a standardised pH meter.

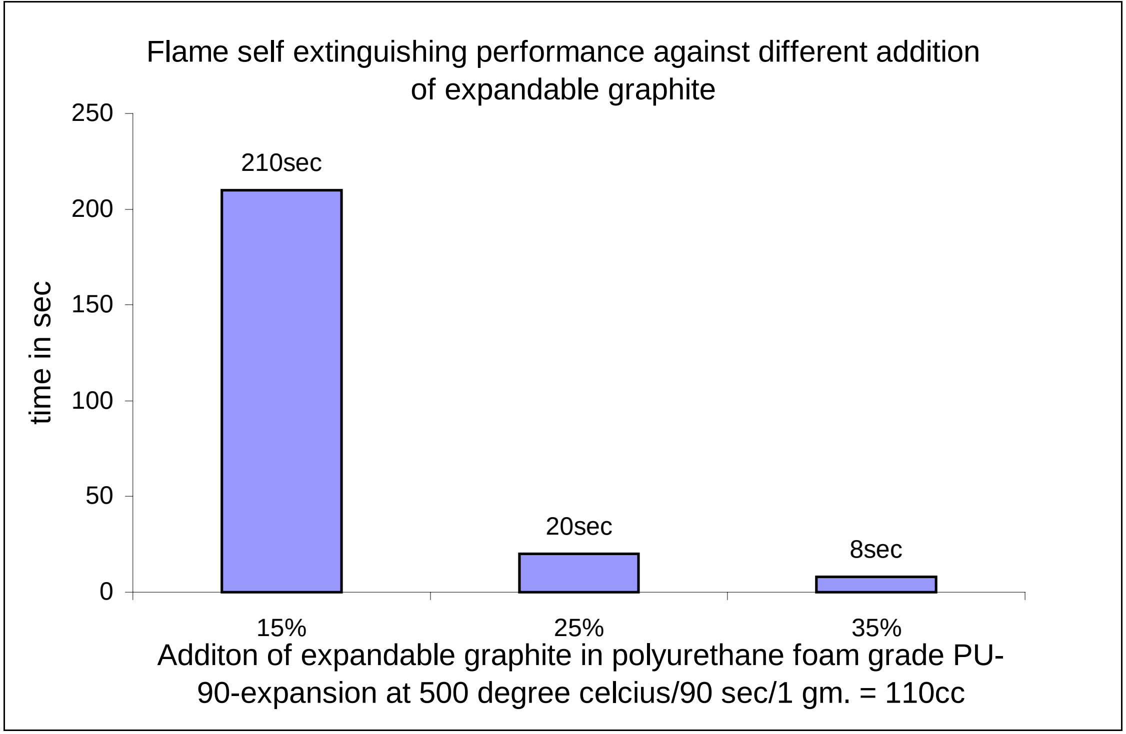
8) *MOISTURE CONTENT* : Place 10 gms. of expandable graphite in a dried pre-weighed watch glass and place in a drying oven at 105^{0}C for one hour. Cool the sample in a desiccator and re-weigh, calculate the percentage of moisture content as follows.

$$\text{Moisture content (\%)} = \frac{\text{Loss in weight of sample (gms)}}{\text{Sample weight (gms)}} \times 100$$

1. Effect of percentage of expandable graphite on the flame self extinguishing time

Various percentage of expandable graphite added in PU foam hence showing flame self extinguishing time.

Graph:7



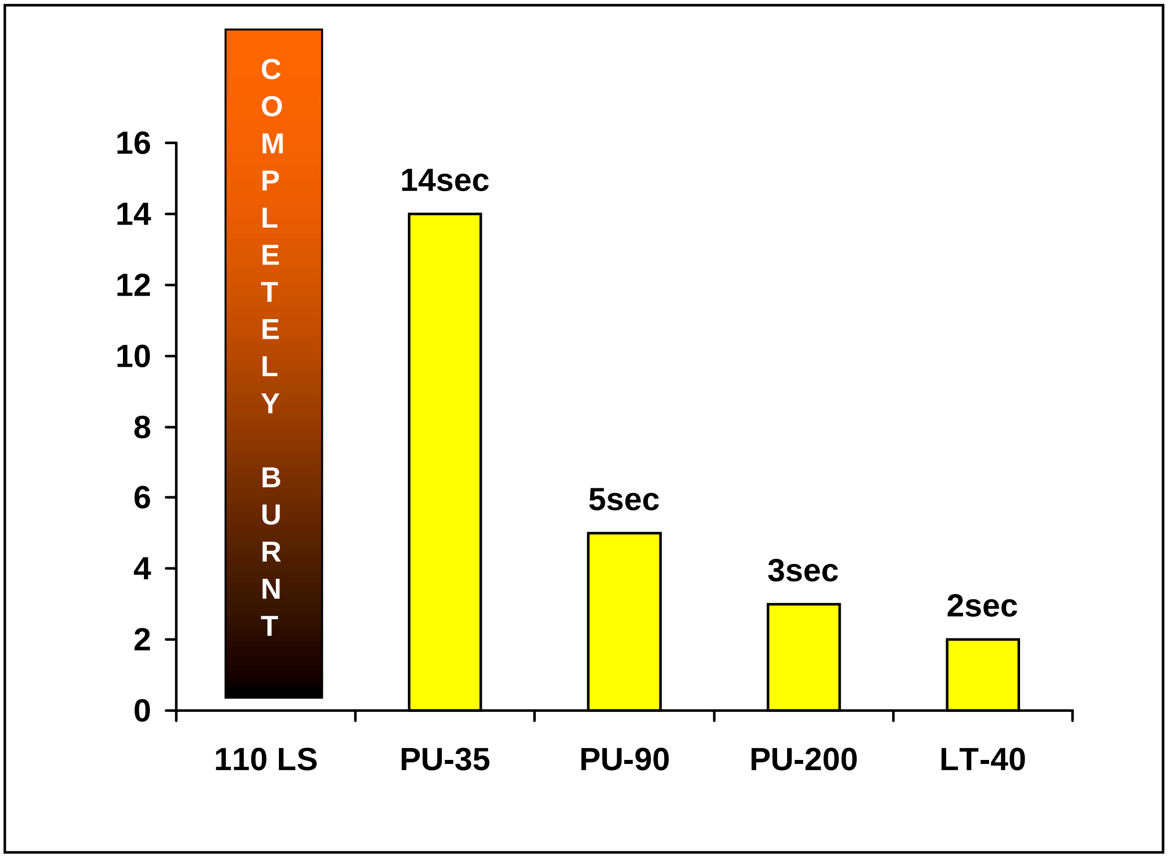
As the addition of expandable graphite increases the flame self-extinguishing, time decreases.

Percentage addition	15%	25%	35%
Burned length	240mm	105mm	100mm
Volume compared with 100% pure polymer	91%	88%	81%

As the addition of expandable graphite, increase the burned length decreases.

2. Flame self-extinguishing time of polyurethane foam with respect to various grades. (Constant addition of 35% of expandable graphite)

Graph: 8



EXPANSION PROPERTY

Exp. at 1000^0C	180 cc	110 **cc**	180 cc	260 cc	275 cc
Exp. at.500^0C	40 cc	38 cc	110 cc	220 cc	240 cc
Exp. at 300^0C	0	8 cc	32 cc	60 cc	80 cc
Exp. at 200^0C	0	0	3 cc	14 cc	28 cc

As the low temperature expansion increases, the flame self-extinguishing time decreases.

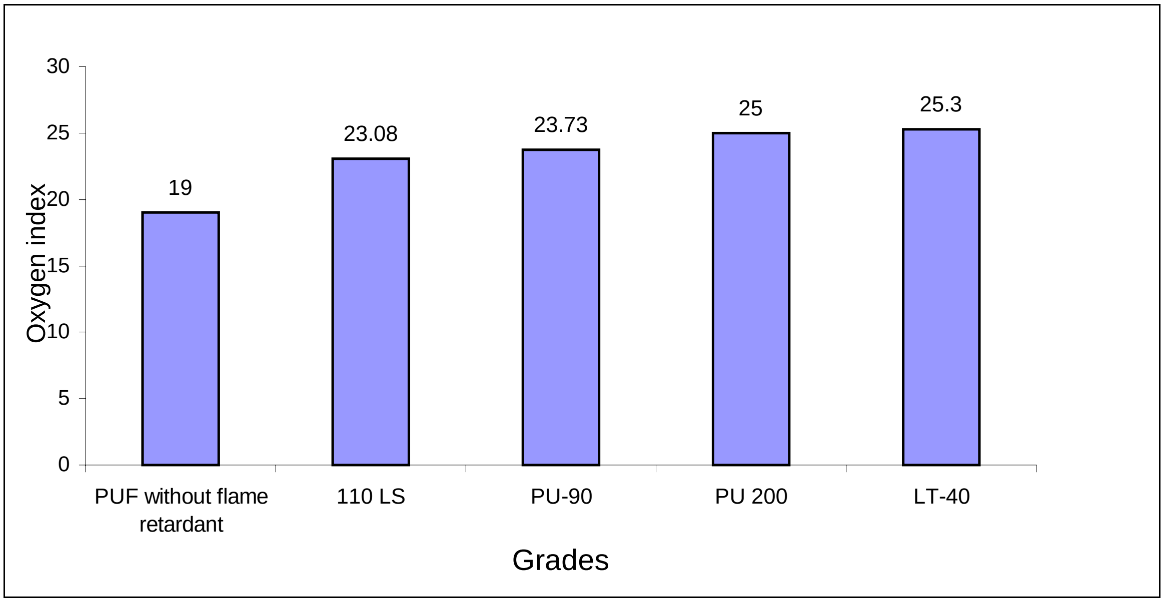
3. Effect of different expansion of expandable graphite of polyurethane foam at constant addition of 35% on oxygen index

GRADES	Oxygen Index
PUF without flame retardant	19.000
Grade 110 LS	23.080
Grade PU-90	23.730
Grade PU-200	25.000
Grade LT-40	25.300

As the low temperature expandable graphite expansion increases, oxygen index increases.

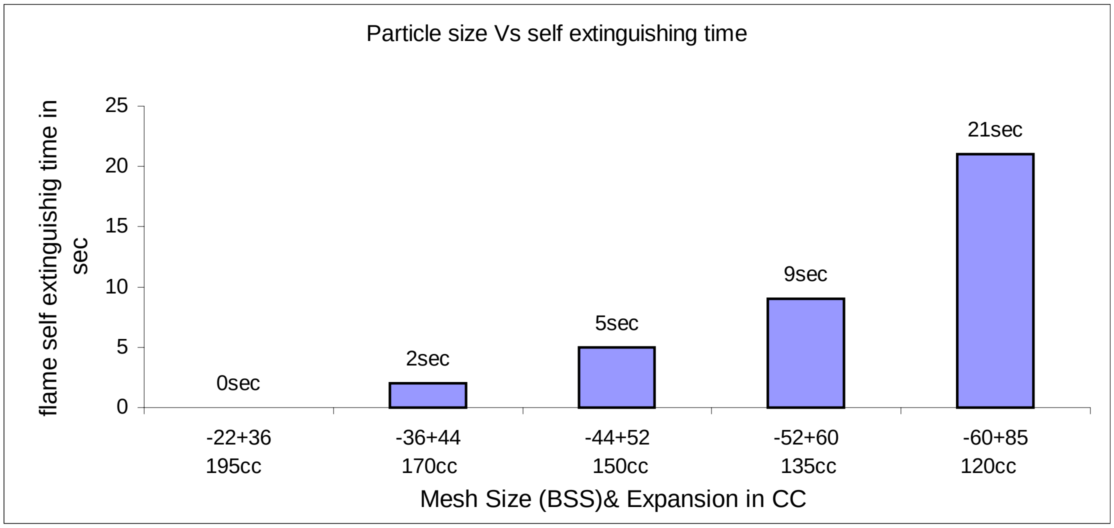
4. Oxygen index of various grades

Graph: 9



5. Effect of particle size of expandable graphite on the flame retardant properties of polyurethane foam (Constant addition of 35% of expandable graphite).

Graph:10

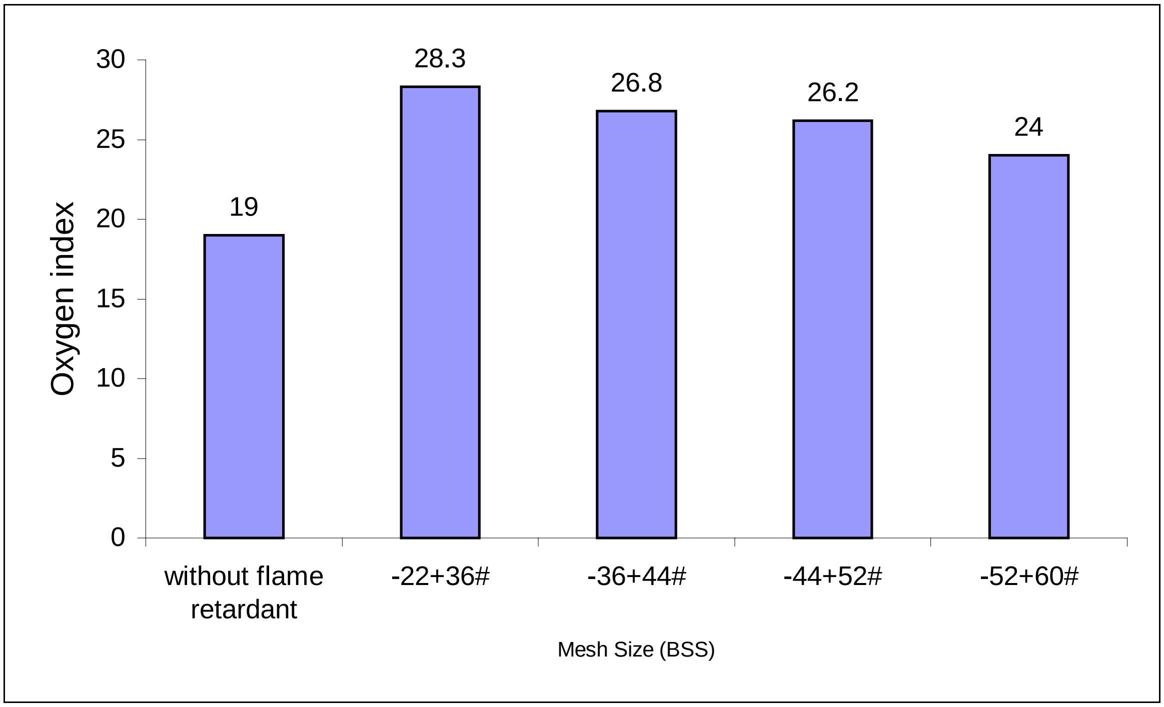


Burned length	80mm	110mm	110mm	115mm	155mm
Mass Loss	0.46%	0.67%	0.857%	1.023%	1.157%
Volume Pure 100% PUF	97.1%	96.1%	88.31%	77.9%	75.32%

As the particle size decreases the flame self-extinguishing time increases and mass loss, burned length increases and the volume of polyurethane foam decreases.

6. Oxygen index with respect to particle size

Graph:11



As the particle size decreases, oxygen index decreases.

7. Relation of expansion oxygen index and volatile matter of expandable graphite on flame extinguishing time.

Table: I : Constant factor: addition of 35% of expandable graphite.

Expandable graphite grades	Expansion at 500^0C/90 sec /min	Oxygen Index	Volatile matter	Flame self extinguishing time
Grade DW-20	9cc	21.30	13.24	Completely burned
Grade 110LS	45cc	23.080	16.00	Completely burned
Grade PU-90	120cc	23.730	22.34	8 sec
Grade PU-200	210cc	25.00	34.77	0-2sec
Grade LT-40	240cc	25.30	36.68	0 sec

As volatile matter increases expansion increases, expansion increases flame extinguishing time decreases and oxygen index increases.

8. Effect of expandable graphite of various grades with respect to burning properties.

Table: II

Grades	Addition	Flame self extinguishing time	Mass loss	Burned length	Melt drip
110LS	35%	Completely burned	71%	Completely burned	Observed
PU-90	35%	7-8 secs	0.87%	105 mm	Not observed
PU-200	35%	0-2 sec	0.86%	90mm	Not observed
LT-40	35%	0sec	0.86%	80mm	Not observed
Melamine	35%	0 sec	1.56%	140mm	Observed
Antimony Trioxide & DBDO (1:3)	35%	22 sec	2.82%	160mm	Observed

Discussion

The fire behaviour of the foam has first been studied by the flame torching method and oxygen index. The result obtained have been showed that increasing amount of expandable graphite employed, the flame retardant performance of polyurethane foam increase that is flame self extinguishing time decreases. It is also have been observed that flame retardant performance increases by the increasing the expansion of expandable graphite.

The most remarkable results obtained by the evolution of low temperature expandable graphite. It has been observed that flame retardant performance mainly depends upon the ability of expandable graphite to expand at the temperature lower than 300°C. the results obtained have showed that increase in low temperature expansion increases the oxygen index of the polyurethane foam incorporated with expandable graphite. Another important parameter has been noticed that by decreasing amount of expandable graphite volume of the polyurethane foam increase.

From the above observation, we suggest a formula for the optimum properties of flame retardance and minimum deterioration on the physical properties of polyurethane foam.

Formula: **T.E = E X Q**

T.E = Total expansion,
E= Expansion of expandable graphite at 500º C,
Q= quantity of expandable graphite used in Polyurethane foam.
For example: Total expansion= 110cc X 35
= **3850cc**

Therefore $\mathbf{Q=\frac{T.E}{E}}$

For example: If the expansion of expandable graphite is 130 cc then the total quantity to be added will be,

$$\frac{3850cc}{130cc} = 29.61 \text{ parts by weight per 100 parts of polyol}$$

It has been observed that if we add the calculated quantity of expandable graphite on the basis of total expansion, the results for the self-extinguishing time are almost same.

9. Total expansion formula

Table : III

Expansion at 500° C/1gm/90 sec	Total expansion Expansion	Quantity in Polyurethane foam	Flame self extinguishing time	Burned length	Volume compared to pure polymer
110cc	$\frac{3850}{110}$	35%	8-9sec	110mm	81%
130cc	$\frac{3850}{130}$	29.61%	8sec	100mm	88%
150cc	$\frac{3850}{150}$	25.66%	7sec	95mm	91.62%
210cc	$\frac{3850}{210}$	18.33%	6sec	90mm	94.5%

It has been observed that we can minimize the effect of filler like expandable graphite on physical properties of polyurethane foam without disturbing flame retardant performance by using formula: expansion X quantity = total expansion and by proper selection of expansion properties of expandable graphite.

Effect of pH and contaminant of expandable graphite on polyurethane foam

While preparing PU Foam with the addition of expandable graphite, preferable pH of expandable graphite should 7 ± 1. If it is less than five pH or more acidic then the free acid react with cross-linking agent, such as amine which will deactivate cross linking in polymerization reaction. Therefore, the amount of amine required for the reaction will decrease and PU Foam will shrink and collapse.

Contaminant: Expandable Graphite should be free from Iron, Copper and Nickel, which can be provide scorching since they greatly accelerate certain oxidation process.

Melt drip: By using flame retardant expandable graphite in polyurethane foam, there is swelling and char formation on the burning surface of polyurethane foam which avoids the melt drip.

Conclusion

1. Flame retardant properties of polyurethane foam improve only by the use of expandable graphite, which expands at lower temperature where polymers start melting, decomposition and ignition.

2. Using total expansion formula can reduce deterioration of physical properties and improves the flame retardant properties of Polyurethane Foam.

3. Stable Polyurethane Foam could be prepared by controlling by parameter of expandable graphite such as pH, contamination with respect to Iron, Copper, and Nickel etc.

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