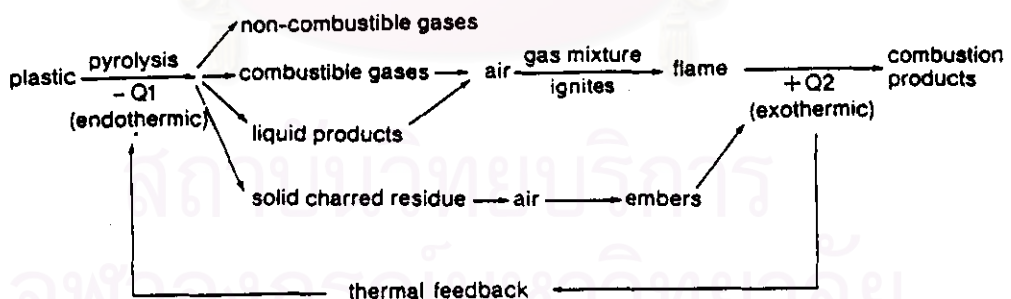# CHAPTER II

THEORY AND LITERATURE REVIEW

The Combustion Process

The combustion of plastics is a process comprising many steps. A simplified schematic representation of the various phenomena which take place during the combustion of plastics is shown in Fig. 2-1

Fig. 2-1 The combustion process

There are 3 necessary states to initiate the actual combustion process of the polymer.

1. Heating

As a material is exposed to a fire and its temperature rises, several phenomena may occur. In thermoplastics, the chain acquire vibration energy, with the bonds becoming more active until the solid becomes a highly viscous liquid. This change occurs at the glass-transition temperature. As the polymer is heated still further, the vibrationally excited bonds begin to break.

The solid plastics is heated by thermal "feedback" or by an external heat sources. In this initial phase thermoplastics tend to soften or melt and start to flow. Thermosetting plastics have a cross-linked molecular structure which prevents softening or melting. If further supply energy, polymer must decompose before vaporising.

2. Decomposition

Decomposition is an endothermic process. As the individual plastics differ in structure, their decomposition temperature-ranges vary within certain limits. Table 2-1 gives the range of decomposition temperatures for some plastics, and for the natural products, cellulose.

Table 2-1 Range of decomposition of some plastics.

Plastic	T_d ($^\circ$C)	Plastic/natural product	T_d ($^\circ$C)
Polyethylene	340 - 440	Polymethyl methacrylate	180 - 280
Polypropylene	320 - 400	Polyacrylonitrile	250 - 300
Polystyrene	300 - 400	Polyamide 6	300 - 350
Polyvinyl chloride	200 - 300	Polyamide 66	320 - 400
Polytetrafluoroethylene	500 - 550	Cellulose	280 - 380

Various decomposition products depending on the constitution of the polymer :

(a) Almost gaseous products are formed ; e.g., the depolymerisation of polymethyl methacrylate results in the formation of over 90% monomer and the degradation of polyethylene leads to the formation of saturated and unstaturated hydrocarbons.

(b) Gaseous products and carbonaceous residues are formed : e.g., the pyrolysis of poly (vinyl chloride) hydrogen polyene sequence forms aliphatics and aromatics in a second step. These escape as gaseous products or remain as solid carbonaceous residues as a result of cross-linking reactions.

(c) Almost carbonaceous residues are formed ; for example in the case of polyacrylonitrile or high temperature resistant plastics such as polyimides.

3. Ignition

The flammable gases formed by pyrolysis mix with atmospheric oxygen, reach the lower ignition limit and are either ignited by an external flame or, if the temperature is sufficiently high, self-ignite. The flash-ignition and self-ignition termperatures of various polymers given in Table 2-2

Table 2-2 Flash-ignition and self-ignition temperatures of various plastics by ASTM D 1029

| Plastic/natural product	Flash-ignition temp. ($^\circ$C)	Self-ignition temp. ($^\circ$C)
Polyethylene	340	350
Polypropylene	320	350
Polystyrene	350	490
Poly (vinyl chloride)	390	450
Polytetrafluoroethylene	560	580
ABS	390	480
Polymethyl methacrylate	300	430
Polyacrylonitrile	480	560
Polyamide 6	420	450
Polyamide 66	490	530
Polyurethane (rigid foam)	310	415
Cotton	210	400

Ignition depends on numerous variables such as oxygen availability, temperature and the physical and chemical properties of the polymer. The reaction of the combustible gases with oxygen is exothermic and, if sufficient energy is available, overrides the endothermic pyrolytic reaction and initiates flame spread. The last state continue from heating, decomposition and ignition is flame spread.

4. Flame spread

A phenomenological description of flame spread along a polymer surface is given in Fig. 2-2. The diffusion flame advances over the decomposed polymer surface.

The other factors which determines the extent of flame spread is the heat of combustion of the polymer.

Fig. 2-2 Schematic of flame spread.
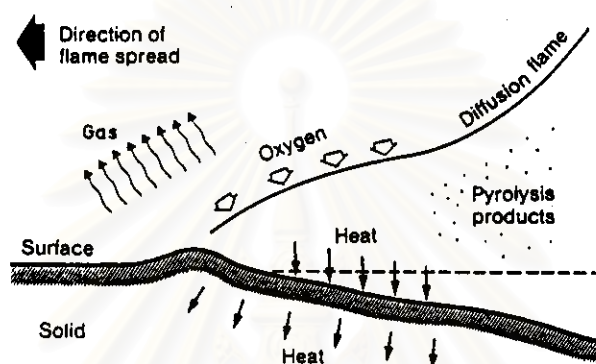
Fire Retarded Mechanism

Fire retarded mechanism of the flame retardant in polymer systems could be grouped into the following three categories :

1. Vapor-Phase Mechanism

In the vapor-phase mechanism, the fire retardants or the modified polymer unit, on heat exposure, release a chemical agent which can remove free-radical intermediates or which can replace the major propagating species. Flame retardation could be implemented by incorporating fire-retardant additives, impregnation the material which a fire-retardant substance, or using fire-retardant comonomers in the polymerization or grafting. Halogenated fire-retardants have been

commonly used in fire-retarding plastics. They are postulated to function by a vapor-phase flame inhibition mechanism which characterized by following criteria :

- Fire-retardant element is lost from the substrate.

- Flame inhibition is insensitive to substrate structure.

- Fire retardance is sensitive to oxidant. (e.g., O_2 or N_2O)

- Fire retardant does not change the composition or amount of volatile.

Halogen-containing flame retardants act by interfering with the radical chain mechanism taking place in the vapor phase. The high-energy $OH^{\cdot}$ and $H^{\cdot}$ radicals formed by combustible gases are removed by the halogen-containing flame retardant. At first the flame retardant breaks down to radicals, where X is Cl or Br.

$$RX \longrightarrow R^{\cdot} + X^{\cdot}$$

The halogen radical $X^{\cdot}$ reacts by hydrogen abstraction from the substrate RH to form hydrogen halide.

$$X^{\cdot} + RH \longrightarrow R^{\cdot} + HX$$
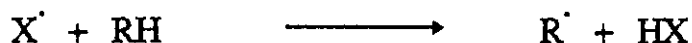
If interferes with the radical chain mechanism by reaction with the high-energy $H^{\cdot}$ and $OH^{\cdot}$ radicals and by replacing them with $X^{\cdot}$ radicals of lower energy. The actual flame retardant effect is thus produced by HX.

$$HX + H^\cdot \longrightarrow H_2 + X^\cdot$$

$$HX + {}^\cdot OH \longrightarrow H_2O + X^\cdot$$
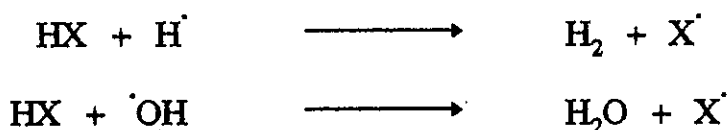
2. Condense-Phase Mechanism

The fire retardants that function by this mechanism have the ability to increase the conversion of polymeric materials to a char residue during heat exposure. The char formed protect the substrate by interfering with the access of oxygen and act as a heat shield for base material.

Phosphorus-containing flame retardants influence mainly the reactions taking place in the condensed phase. They are particularly effective in materials which high oxygen content, such as oxygen-containing plastics as well as cellulose and its derivatives. Many of the phosphorus compounds are liquid and possess plasticizing properties.

The following are the indicators of a condensed-phase operation for a fire retardant :

- Fire-retardant results in enhanced char formation.

- Fire-retardant elements is retained in the substrate.

- Fire-retardant elements is often ineffective in the vapor phase.

- Fire retardance is sensitive to the substrate structure.

- Fire retardance is sensitive to oxidant (e.g., O_2 or N_2O)

- Fire retardant changes the composition of volatiles.

3. Miscellaneous Mechanism

Apart from vapor-phase and condensed-phase mechanisms, fire retardants could also function in a number of other ways. The following are some other alternative model of flame inhibition :
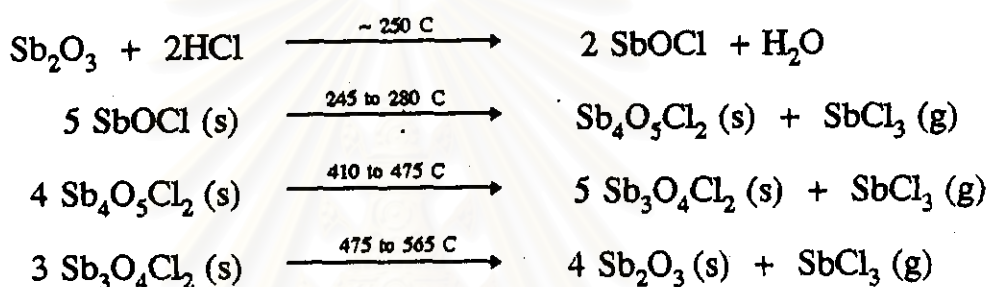
- Large volumes of noncombustible gases produce which can dilute oxygen supply to flame and/or dilute the fuel concentration.

- The fire retardant may act as a thermal sink to increase the heat capacity of the combustion system or to reduce the fuel content to a level below the lower limit of flammability.

- The endothermic decomposition of the fire retardant could lower the polymer surface temperature and retard pyrolysis of the polymer.

Synergism

The quantitative relationship of flammability of a polymer which respect to the concentration of fire retardant is usually not linear, and there is no logical reason to expect combinations of different fire retardants to show a linearly additive result either. The effect of a mixture of two or more fire retardants is often found to be "synergistic" or "antagonistic". Synergism is the case in which the effect of two or more components taken together is greater than the sum of their individual effects and can lead to less expensive polymer system.

One of the sample antimony trioxide-halogen synergism : in polymer systems containing antimony trioxide (Sb_2O_3) and halogen, the

most important reactions take place in the gas phase. They are the result of an effect on the radical chain mechanism. Antimony trioxide reacts with hydrogen chloride and forms antimony trichloride and various antimony oxychlorides, which act as radical interceptors like HCl or HBr to yield an intermediate SbOCl which is actually the effective agent. The formation of SbOCl has been illustrated by the following equations :

$$Sb_2O_3 + 2HCl \xrightarrow{\sim 250\ C} 2\ SbOCl + H_2O$$

$$5\ SbOCl\ (s) \xrightarrow{245\ to\ 280\ C} Sb_4O_5Cl_2\ (s) + SbCl_3\ (g)$$

$$4\ Sb_4O_5Cl_2\ (s) \xrightarrow{410\ to\ 475\ C} 5\ Sb_3O_4Cl_2\ (s) + SbCl_3\ (g)$$

$$3\ Sb_3O_4Cl_2\ (s) \xrightarrow{475\ to\ 565\ C} 4\ Sb_2O_3\ (s) + SbCl_3\ (g)$$

Char Formation

In the majority of fire situations materials change the mode of burning to effectively improve flame retardancy and reduce smoke emission by the promotion of a carbonaceous char. There are several approaches for improving the yield and integrity of char or for producing barrier layers.

Carbonaceous char barriers may be formed by the normal mode of polymer burning, and besides representing a reduction in the amount of material burned, the char may act as a fire barrier. Table 2-3 showed that a 1 mm. layer would keep an underlying substrate from reaching ignition

temperature when the external fire atmosphere was at 743°C, and a 2.7 mm. layer would suffice when the fire atmosphere was 1500°C.

For polymers with low char-forming tendencies, such as polyolefins, one approach to obtain adequate char is to add a char-forming additive.

Table 2-3 Effect of closed-cell char foam in preventing a substrate from reaching ignition temperature (300°C)

Thickness (mm.)	External Temp. ($^\circ$C)
0.1	342
1.0	743
2.7	1500
10.0	4600

Flame Retardants

There is general agreement that plastics cannot be made fireproof. Plastics are organic-based materials and will burn under the proper conditions. However, the susceptibility to fire can be reduced, and the spread of flame can be decreased by the incorporation of additives. Additives called "flame retardants" help reduce the ignition of the plastic and the rate of flame propagation.

An ideal flame retardant should be :

1. Easy to incorporate in plastics

2. Compatible with the plastics (not bleed out)

3. Not alter its mechanical properties

4. Colorless and odorless

5. Good light stability

6. Good heat stability

7. Resistant to aging and hydrolysis

8. Matched to the decomposition temperature of the polymer. (Its effect .must begin below the decomposition temperature of the plastics and continue over the whole range of its decomposition)

9. Must not cause corrosion

10. Effective in small amounts

11. Without harmful physiological effects

12. Must also emit only low level of smoke and toxic gases

13. Cheap cost and possible to use

Generally flame retardants classified into 2 basic types :

- **Organic flame retardants** are almost exclusively plasticizers.

- **Inorganic flame retardants** can be subdivided as follows :

: Antimony compounds and extended products.

: Metal hydroxides, hydroxycarbonates, and carbonates.

: Molybdenum, zinc, and iron compounds

1 Antimony Compounds and Extended Products.

Antimony compounds are the most commonly used flame retardants for PVC. Because of their efficiency in reducing flame spread at low level

without any major effect on physical properties. Antimony compounds must work in combination with a halogen-containing compounds.

1.1 Antimony Trioxide

This is the most populary used and cost efficiency as the primary antimony flame retardant. Typical properties are shown in Table 2-4

TABLE 2-4 Typical Properties of Antimony Trioxide

Molecular weight	291.52
Melting point	1213°F (656°C)
Specific gravity at $20/20^\circ$C	5.5
Physical form	Fine white powder
Crystal type	Cubic (major)
Average particle size	1 micron
Antimony (as metal)	83.1%
Arsenic %	0.1-0.3%
Lead	0.05-0.2%
Iron	<0.002%

Antimony oxide (antimony trioxide) has very little fire-retardant activity when used by itself but performs synergistically with halogens. One theory holds that antimony oxychloride is formed during burning, and that this is the active fire-retardant. With PVC, the chlorine in the polymer itself supplies this function.

Antimony trioxide has small (0.1-2.0 microns) particle size, it can effect on physical properties of PVC same as calcium carbonate filler of similar particle size. It has a high refractive index compared to PVC,

combined with its fine particle size, gives it high pigmentary properties of white pigment, but does not has screening action on UV light same as titanium dioxide. Antimony trioxide is considered and adverse effect to bright colors, because it necessary to use higher levels of expensive pigments to achieve the desired color.

Flame retardancy is controlled by the antimony content. The majority of antimony trioxide used is a fine dusty powder. There is a growing concern and awareness of the hazards from all dusts. To avoide this hazard, can use low or non-dusting forms of antimony trioxide.

Manufacturers of antimony trioxide in the United States and Western Europe are shown in Table 2-5

TABLE 2-5 Major Manufacturers of Antimony Trioxide

Manufacturer	Location	Trade name
		United States
Amspec Chemical	Gloucester City, NJ	Amstar
Anzon Inc	Philadelphia, PA	TMS
Asarco	New York, NY	
Laurel Industries	Cleveland, OH	Fire Shield
Elf Atochem N.A.	Philadelphia, PA	Thermoguard
		Western Europe
Campine	Brussels, Belgium	Antiox
Cookson Minerals Ltd	Newcastle, England	Timinox
La Lucette	Paris, France	Triox
Sica	Chauny, France	Naige
Stibiox	Hungerkamp, Germany	

1.2 Combination Products

Numerous combination products, consisting of antimony trioxide, synergists, and extenders, are commercially available. Another word of caution is that many of the combination products work by acting as char formers by introducing a compound based on a transition element, such as zinc, iron, molybdenum, etc. In some instances, these products can adversely effect color and heat stability of the PVC compounds.

Manufacturers of antimony trioxide combination products are shown in Table 2-6

TABLE 2-6   Manufacturers of Antimony Trioxide Combination Products

Manufacturer	Trade name	Chemical type	Specific gravity
Anzon Inc.	AZ-11	Sb-Mg-Zn	4.9
Anzon Inc.	AZ-12	Sb-Si-Mg-Zn	4.3
Anzon Inc.	AZ-20	Sb-Zn-P	4.5
Anzon Inc.	Smokebloc Eleven	Sb-Mo-Ca	3.9
Anzon Inc.	Smokebloc Twelve	Sb-Mo-Ca	3.5
Anzon Inc.	Oncor 55	Sb-Si-Mg	3.6
Anzon Inc.	Oncor 75RA	Sb-Si-Mg	3.3
Elf Atochem North America	Thermoguard CPA	Sb-Ba-Zn	4.9
Elf Atochem North America	Thermoguard WE	Sb-Ba-Zn	4.9
Laurel Industries	LSFR	Sb-Zn-Ca	4.5

1.3 Other Antimony Compounds

Antimony Pentoxide This product finds limited application in PVC when clarity is of prime importance. Cost is typically about three times the base antimony trioxide price. The specific gravity of antimony pentoxide is 3.8

Manufacturers of antimony pentoxide are shown in Table 2-7

TABLE 2-7 Manufacturers of Antimony Pentoxide

Manufacturer	Trade name (grade)
Laurel Industries	TPL
PQ Corporation	Nyacol ZTA
PQ Corporation	Nyacol ADP-480
PQ Corporation	Nyacol A1530
PQ Corporation	Nyacol A1550

Sodium Antimonate As is the case with antimony pentoxide, this product also limited application in transparent PVC. Cost per pound of sodium antimonate is between the trioxide and ten pentoxide. The specific gravity of sodium antimonate ($NaSbO_3$) is 4.8

Manufacturers of sodium antimonate are shown in Table 2-8

TABLE 2-8 Manufacturers of Sodium Antimonate

Manufacturer	Trade name and grade	Particle size (micron)
Anzon Inc.	Fyrebloc SAP2	2
Anzon Inc.	Fyrebloc SAP5	5
Elf Atochem N.A.	Thermoguard FR	1

2. Metal Hydroxides, Hydroxycarbonates, and Carbonates.

Alumina trihydrate and alkaline earth metal derivatives provide flame retardancy by releasing water or, in the case of carbonates CO_2 as well, to quench the flame. In PVC applications, alkaline earth-based can act as acid scavengers, reducing HCl evolution and smoke emission.

Current commercial products are either aluminum or magnesium compounds and can be subdivided as follow :

2.1 Alumina Trihydrate (ATH)

ATH is the lowest cost of this class of products and widest application. ATH has low decomposition temperature (initial water release is around 204°C). Manufacturers of ATH are shown in Table 2-9

TABLE 2-9 Suppliers of Alumina Trihydrate

Company	Location	Trade name / grade	End uses[a]
Alcan Chemicals	Cleveland, OH	Baco FRF 20	FF, CF
Alcan Chemicals	Cleveland, OH	Baco FRF 80	FS
Alcan Chemicals	Cleveland, OH	Baco FRF 85	CVB
Alcan Chemicals	Cleveland, OH	Baco LV2	FF
Alcan Chemicals	Cleveland, OH	Baco Superfine 4	CVB, CF, R
Alcan Chemicals	Cleveland, OH	Baco Superfine 7	W, CF, R
Alcan Chemicals	Cleveland, OH	Baco Superfine 11	R
Aluchem, Inc.	Reading, OH	AC-400K	FS
Aluchem, Inc.	Reading, OH	AC-712K	W, PG, R
Aluchem, Inc.	Reading, OH	AC-714K	FS, PG, R
Aluchem, Inc.	Reading, OH	AC-722K	FS, PG, R
Alcoa Industries Chemical Division	Bauxite, AR	Hydral 710	R
Custom Grinders Sales	Chatsworth, GA	Polyfill 402	CF, CVB
Custom Grinders Sales	Chatsworth, GA	Polyfill 502	W
Pluess-Staufer International	Stamford, CT	Martinal OL-104/C	W
Pluess-Staufer International	Stamford, CT	Martinal OL-104/LE	W
Pluess-Staufer International	Stamford, CT	Martinal OL-107/C	W
Pluess-Staufer International	Stamford, CT	Martinal OL-107/LE	W
Pluess-Staufer International	Stamford, CT	Martinal OL-111/LE	W
Nyco	Willsboro, NY	21 Nycoat 10734	W
Solem Industries	Norcross, GA	Micral 855SL	W, R
Solem Industries	Norcross, GA	SB-432	FS, PG
Solem Industries	Norcross, GA	SB-632	FS,PG,FF,R,W
Solem Industries	Norcross, GA	Micral 932	FS, PG, W

[a] CF-coated fabrics; CVB-conveyor belts (mines); FF-foamed flooring; FS-film and sheeting; PG-plastisols, general; R-rigids; W-wire and cable

2.2 Magnesium Compounds

Magnesium hydroxide, magnesium hydroxycarbonate, magnesium-calcium carbonate, and mixtures of these compounds function in a manner similar to ATH and sometimes used replacements for ATH, but more expensive than ATH. When evaluating different types of magnesium compounds it is important to compare their overall properties and cost efficiency and not just their price per pound because activity of these products can vary considerably.

Manufacturers of magnesium compounds are shown in Table 2-10

TABLE 2-10 Manufacturers of Magnesium Compounds

Manufacturer	Location	Trade name (grade)	Particle (μm)	SpGr.20°C
Magnesium Hydroxide				
Dow	Midland, MI	MHT-100	-	2.4
Martinswerke	Bergheim, Ger.	VP8812	0.9	2.4
Martinswerke	Bergheim, Ger.	VP8813	0.9	2.4
Martinswerke	Bergheim, Ger.	VP8814	0.9	2.4
Martinswerke	Bergheim, Ger.	VP8817	0.9	2.4
Morton International	Danvers, MA	Versamag UF	1.0	2.4
Steetley Quarry Products	Hartlepool	Mycal	-	2.4
Solem Industries	Norcross, GA	Zerogen 10	2.2-2.8	2.4
Solem Industries	Norcross, GA	Zerogen 30	0.8-1.2	2.4
Hydrated Magnesium Carbonates (and Hydrated Mg-Ca Carbonates)				
Microfine Minerals, Ltd.	Raynesway	Ultracarb U5	0.5	2.5
Microfine Minerals, Ltd.	Raynesway	Ultracarb C5-10	0.5	2.5
Microfine Minerals, Ltd.	Raynesway	Ultracarb P5-20	0.5	2.5
Microfine Minerals, Ltd.	Raynesway	Ultracarb L5-20	0.5	2.5
Morton International	Danvers, MA	Elastocarb UF	1.0	2.2
Properietary Magnesium Compounds				
Solem Industries	Norcross, GA	Zerogen 15	2.2-2.8	2.2
Solem Industries	Norcross, GA	Zerogen 35	0.8-1.2	2.2

3. Molybdenum, Zinc, and Iron Compounds.

Metal compounds can catalyze the dehydrochlorination of PVC, for this reason such material are usually avoided in PVC due to their effect on thermal stability. It promotes char which generally improves flame retardancy and smoke suppression.

3.1 Molybdenum Compounds

Many molybdenum compounds have been found to be potential char formers in PVC compositions and as such provide both flame-retardant and smoke-suppressant properties. The main drawback of molybdenum compounds is their relatively high cost.

3.2 Zinc Compounds

Zinc compounds such as zinc borate used as a combination flame retardant and smoke supperssant. However, it does have a notable effect on heat stability. Other zinc compounds, including zinc oxide, also has a detrimental effect on heat stability.

Manufacturers of molybdenum and zinc flame retardants (and smoke suppressants) are shown in Table 2-11

3.3 Iron Compounds

Many iron compounds act as both flame retardants and smoke suppressants in PVC. Their main disadvantages are that they have an effect on heat stability and highly pigmentary.

TABLE 2-11   Manufacturers of Molybdenum and Zinc Flame Retardants and Smoke Suppressants

Manufacturer	Location	Trade name	Composition	Size (μm)	Sp.Gr.
Alcan Chemicals	Cleveland, OH	Flamtard H	Zinc hydroxystannate	2.5	3.3
Alcan Chemicals	Cleveland, OH	Flamtard S	Zinc stannate	1.7	3.9
Anzon Inc.	Philadelphia	Ongard 2	Mg-Zn complex	1.5	4.4
Anzon Inc.	Philadelphia	Smokebloc 11	Sb-Mo complex	1.9	3.9
Climax Specialty Metals	Cleveland, OH	POL-U	MoO_3	2.5	4.69
Climax Specialty Metals	Cleveland, OH	AOM	$(NH_4)_4Mo_8O_{26}$	1	3.18
Climax Specialty Metals	Cleveland, OH	ZB-112	$ZnO\ B_2O_3\ 2H_2O$	6	2.50
Climax Specialty Metals	Cleveland, OH	ZB-223	$2ZnO\ 2B_2O_3\ 3H_2O$	4	2.83
Climax Specialty Metals	Cleveland, OH	ZB-237	$2ZnO\ 3B_2O_3\ 7H_2O$	2.6	2.31
Climax Specialty Metals	Cleveland, OH	ZB-325	$3ZnO\ 2B_2O_3\ 5H_2O$	2	2.66
Climax Specialty Metals	Cleveland, OH	ZB-467	$4ZnO\ 6B_2O_3\ 7H_2O$	5	2.74
Sherwin Williams	Cleveland, OH	Kemgard 981	ZnO-phosphate complex	1	4.2
Sherwin Williams	Cleveland, OH	Kemgard 425	Ca-Zn molybdate-ZnO	1.9	3.0
Sherwin Williams	Cleveland, OH	Kemgard911A	Ca-Zn molybdate-ZnO	1.9	3.0
Sherwin Williams	Cleveland, OH	Kemgard911B	$ZnMoO_4$-ZnO	0.7	5.06
Sherwin Williams	Cleveland, OH	Kemgard911C	$ZnMoO_4$ on talc	10	2.8
Sherwin Williams	Cleveland, OH	Kemgard911T	$ZnMoO_4$ on talc	10	2.8
U.S. Borax	Los Angeles	Firebrake ZB	$2ZnO\ 3B_2O_3\ 5H_2O$	-	2.8
U.S. Borax	Los Angeles	Firebrake ZB*	$2ZnO\ 2B_2O_3\ 5H_2O$	-	2.8

*Firebrake ZB (fine)

Flame Retardants for PVC

Although poly (vinyl chloride) (PVC) resin is inherently fire-retardant by itself, PVC is fire-retardant due to its high chlorine content approximately 57%. When PVC is compound with diester plasticizers and other modifiers, the resultant compositions can act as combustible fuels for

fire propagation. In this case flexible poly (vinyl chloride) want some additive which called flame retardant to improve flammability property. Flame-retardancy is readily restored by adding various solid or liquid additives, chiefly those containing chlorine, phosphorus, or antimony.

There are three approaches to improving the flame and/or smoke resistance of flexible PVC :

1. Use of inorganic additives as mention above.
2. Use of flame-retardant plasticizers as partial or complete replacements for conventional plasticizers.
3. A Combination of 1 and 2.

Flame Retardant Plasticizers

The principal flame-retardant PVC plasticizers are triaryl phosphates and alkyl diaryl phosphates. Other types include various chlorinated paraffins, used mainly in Europe.

Phosphate Plasticizer Types

All phosphate plasticizers used in flexible PVC are derived from phosphorus oxychloride. The general structure is

$$(R_1O)(R_2O)(R_3O)P=O$$
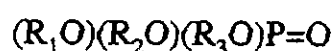
where R_1, R_2, and R_3 may be alkyl or aryl, or R_1 may alkyl and R_2 and R_3 aryl.

Triaryl Phosphates In the family of triaryl phosphates, tricresyl phosphate (TCP) was the industry standard for many years. TCP had low volatility compared with triphenyl phosphate (TPP) and TCP also had the advantage of being liquid at room temperature.

Commercial TPP has a freezing point of 48.3°C minimum and tends to crystallize out of PVC unless used at relatively low phr in combination with a high solvating plasticizer. Because of this and its high volatility , TPP finds only limited (5 phr) use in flame-resistant PVC.

TCP effective flame retardant but costly, has poor light stability and diminish cold impact strength.

Trialkyl Phosphates Tri-2-ethylhexyl phosphate (TOF or TOP) is the only trialkyl phosphate that has achieved any success in PVC formulating, and this has been more for its value as a low-temperature plasticizer than as a flame retardant.

Alkyl Diaryl Phosphates   The commercially available alkyl diaryl phosphates represent a balance in efficiency, volatility, and low-temperature properties between TOF and the triaryl phosphates. One of this class of plasticizers, 2-ethylhexyl diphenyl phosphate, has been regulated by the U.S.Food and Drug Administration for use in adhesives and packaging applications.

Most of phosphate plasticizers used in PVC compounding have phosphorus contents in the range 7.8-8.6%. Composition and suppliers of triaryl phosphates are shown in Table 2-12

Table 2-12 Composition and Suppliers of Triaryl Phosphates

Supplier	Trade name	Composition	Molecular weight	%P
Akzo Chemical	Phosflex Lindol	Tricresyl phosphate	368	8.4
Akzo Chemical	Phosflex 179A	Trixylenyl phosphate	400	7.8
Akzo Chemical	Phosflex TPP	Triphenyl phosphate	326	9.5
Akzo Chemical	Phosflex 41P	.	391	7.9
Akzo Chemical	Phosflex 51B	.	380	8.2
Akzo Chemical	Phosflex 61B	.	388	8.0
Akzo Chemical	Phosflex 71B	.	364	8.5
Akzo Chemical	Phosflex 72B	.	.	.
Albright & Wilson	Pliabrac TCP	Tricresyl phosphate	.	8.3
Albright & Wilson	Pliabrac TXP	Trixylenyl phosphate	.	7.6
Albright & Wilson	Pliabrac 519	.	.	8.3
Albright & Wilson	Pliabrac 521	.	.	8.1
Albright & Wilson	Pliabrac 524	.	.	7.7
Ciba Geigy	Reofos 50	.	.	.
Ciba Geigy	Reofos 65	.	.	.
Ciba Geigy	Reofos 95	.	.	.
FMC Corporation	Kronitex TCP	Tricresyl phosphate	370	8.4
FMC Corporation	Kronitex TXP	Trixylenyl phosphate	400	7.8
FMC Corporation	Kronitex 50	.	375	8.3
FMC Corporation	Kronitex 75	.	373	8.3
FMC Corporation	Kronitex 100	.	390	7.9
FMC Corporation	Kronitex 200	.	420	7.4
Monsanto Company	Santicizer 154	.	371	8.4

Compositions of alkyl diaryl phosphate, phosphate blends, and trioctyl phosphate are shown in Table 2-13

General Performance of Phosphates in PVC

Phosphates are normally used as partial replacements for general-purpose (GP) phthalates and other ester-type plasticizers.

The alkyl diaryl phosphates are clearly superior to the triaryl phosphates in efficiency and lower in specific gravity (advantages for high-priced plasticizers). They are also superior in low-temperature flexibility. The triaryl phosphates are generally lower in volatility.

Phosphates show excellent solvency for PVC and can be used to lower processing temperature or shorten processing time. But they are held to the lowest level to minimize cost.

Table 2-13   Composition of Alkyl Diaryl Phosphates, Phosphate Blends, and Trioctyl Phosphate

Composition	Registered trade name	Molecular weight	% P
2-Ethylexyl diphenyl phosphate	Phosflex 362	362	8.5
2-Ethylexyl diphenyl phosphate	Santicizer 141	362	8.6
Isodecyl diphenyl phosphate	Phosflex 390	390	7.9
Isodecyl diphenyl phosphate	Santicizer 148	390	7.9
Blend of isodecyl diphenyl phosphate and t-butylphenyl diphenyl phosphate	Phosflex 370	370	8.4
Modified triaryl phosphate (blend)	Santicizer 143	.	8.3
Tri-2-ethylhexyl phosphate (trioctyl phostate)	Kronitex TOF	434	7.1
Tri-2-ethylhexyl phosphate (trioctyl phostate)	Tolplaz TOF[a]	.	7.1

[a] Toplaz from Albright & Wilson

Chlorinated Paraffins

Chlorinated paraffins used in PVC compounding typically have chlorine contents in the range of about 45-60%. Manufacturers and physical properties of commercial products are shown in Table 2-14

Table 2-14   Composition and Typical Physical Properties of Chlorinated Paraffins

Registered trade name	Supplier	% Cl	Molecular weight	Viscosity (cP, 25°C)	Color APHA
Cereclor S45	ICI	45	390	200	80
Cereclor S52	ICI	52	440	1,500	100
Cereclor S58	ICI	58	500	35,000	150
FLX-0007	Witco	45	.	350	3[a]
FLX-0002	Witco	50	.	300	1[a]
FLX-0005	Witco	53	.	680	2[a]
FLX-0008	Witco	53.5	.	1,500	3[a]
FLX-0023	Witco	55	.	5,500	3[a]
FLX-0018	Witco	55	.	45,000	2[a]
Doverguard-152	Dover	51	.	1,500	1[a]
Doverguard-5761	Dover	59	.	2,000	1[a]

[a] Gardner color scale

General Performance of Chlorinated Paraffins in PVC

Chlorinated paraffins are used as secondary plasticizers, mainly to lower compound volume cost. Additional cost-lowering benefits may be achieved with chlorinated paraffins in certain flame- and smoke-resistant compounds and have a low order of toxicity. On the other hand, they have an adverse effect on high-temperature and UV-light stability of PVC

compounds, and the higher-chlorine-content grades reduce low-temperature flexibility. Care is required to limit temperature in storage since the chlorinated paraffins tend to discolor when stored at temperature in excess of 95-104°F (35-40°C).

Compatibility limits of blends of chlorinated paraffins and ester-type plasticizers require special attention in formulating PVC compounds. For example, limits for a blend of Cereclor S52 (52% Cl) with DOP in a PVC compound are shown in Figure 2-3

Figure 2-3 Compatibility limits for chlorinated paraffin (52% Cl) in PVC compounds (DOP plasticizer).
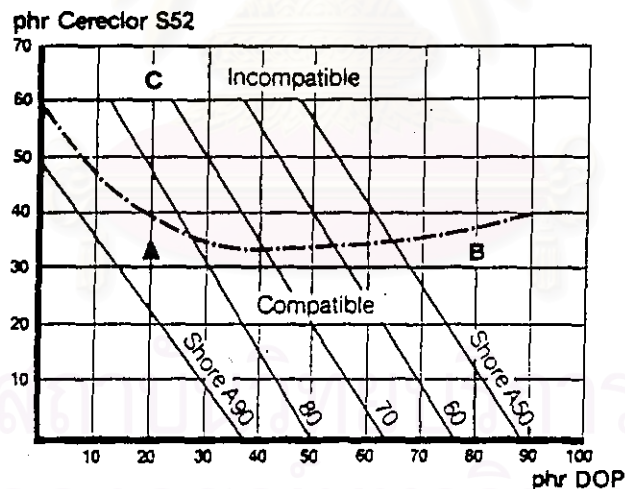
Increasing chlorine content of chlorinated paraffins increases compatibility as shown in Figure 2-4

Figure 2-4 Compatibility limits for chlorinated paraffins in PVC compounds

phr Cereclor

Incompatible

Cereclor S58
Cereclor S52
Cereclor S45

Compatible

phr DOP
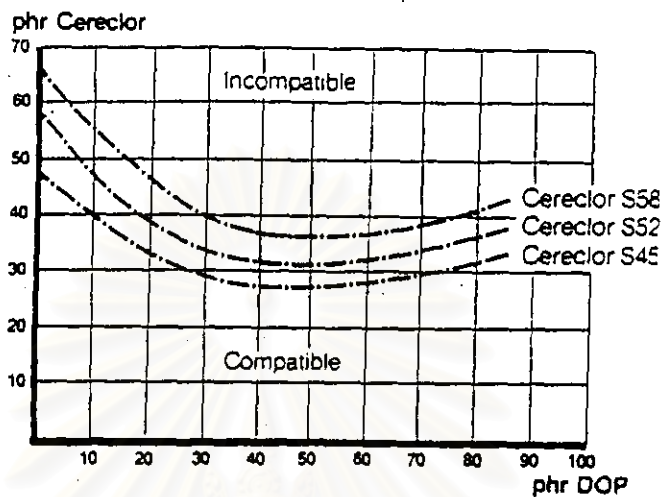
Development of Inorganic Tin Compounds as Flame Retardant

At the present time, inorganic tin compounds find a relatively small use in natural polymers, particularly for woolen rugs and sheepskins. Although certain other metal derivatives have received more attention, there has been much interest recently in the potential use of tin chemicals as flame retardants and smoke suppressants for synthetic polymers.

In view of the current demand for novel, non-toxic flame- and smoke-suppressant systems for synthetic polymers, certain inorganic tin compounds have been evaluated as fire retardants in a number of plastic and elastomeric substrates. The results obtained indicate that tin compound additives, in particular, zinc hydroxystannate and zinc stannate, exhibit beneficial properties both in halogenated and halogen-free formulations.

Inorganic tin compounds, in particular, zinc hydroxystannate and zinc stannate, are effective fire retardants in a number of polymer systems. They appear to have advantages over certain existing commercial additives, namely :

1) Non-toxicity

2) No discoloration of substrate

3) Effective at low levels

4) Little apparent effect on mechanical properties

5) Flame-retardant synergism with halogens and/or alumina trihydrate

6) Smoke suppression

7) Decrease in carbon monoxide production

8) Wide range of applicability

Some important properties of zinc hydroxystannate (ZHS) and zinc stannate (ZS) are show in Table 2-15

Recent studies at International Tin Research Institute (ITRI), carried out in collaboration with external organisations, have shown that certain inorganic tin additives, including SnO_2 , $ZnSn(OH)_6$ and $ZnSnO_3$, are effective flame- and smoke-retardants in a range of chlorinated polymers, including rigid PVC, flexible PVC and neoprene.

Hence, it is apparent that certain inorganic tin compounds are very effective flame retardants and smoke suppressants for halogenated polymer formulations. Since these additives are generally non-toxic, their potential

use as partial or total replacements for existing commercial flame retardants, such as antimony trioxide, is thought to merit serious consideration.

Table 2-15 Properties of zinc hydroxystannate and zinc stannate

Item	ZHS	ZS
Chemical formula	$ZnSn(OH)_6$	$ZnSnO_3$
CAS No.	1202-96-2	12036-37-2
Appearance	white powder	white powder
Analysis (approx.) : Sn	41%	51%
Zn	23%	28%
Cl	<0.1%	<0.1%
free H_2O	<1%	<1%
Specific gravity	3.3	3.9
Decomposition temp. ($^\circ$C)	>180	>50
Toxicity	very low	very low

Thermogravimetry Analysis (TGA)

Thermogravimetry (the thermobalance) is an instrument that permits the continuous weighing of a sample as a function of temperature. The sample may be heated or cooled at some selected rate or it may be isothermally maintained at a fixed temperature. Perhaps the most common mode of operation is heating the sample at furnace heating rates from 5 to $10^{\circ}C\ min^{-1}$. The modern thermobalance generally consists of the following component parts : (a) recording balance; (b) furnace; (c) furnace temperature programmer or controller; and (d) recorder.

The most important component of the thermobalance is the recording balance. Requirements for suitable recording balance are essentially those for a good analytical balance, i.e., accuracy, precision, sensitivity, capacity, resistance to corrosion, rugged construction, and insensitivity to ambient temperature changes. From a practical viewpoint, the balance should be simple to operate and versatile so that it can be used for varied applications. The restoring force is applied as a current passing through a coil which interacts with a magnetic field. This change in electrical current (or voltage) is proportional to the change in mass of the sample and can be recorded. Also, the analog signal output of the balance can be converted to a derivative of the mass change or digitized by an analog-to-digital converter for data processing by digital computers. If real-time computer processing is applied, a wide variety of on-stream

process controls with feed-back loops to control the experimental parameters and data collection are possible.

Numerous sample containers are available for containment of the sample in a thermobalance. The type employed usually depends on the nature, amount, and reactivity of the sample and the maximum temperature desired. Common materials of construction include alumina, platinum, platimum-10% rhodium, aluminum, quartz, glass, nickel, tungsten, and graphite. Sample sizes range from 1 to 20 mg, depending on the sample's density.

A wide variety of furnaces are available for thermobalances, each designed for a specific temperature range from -150°C to over 2800°C. Most of the furnaces have resistance heater elements, but some employ infrared heating for extremely rapid heating and cooling rates. No one furnace design can be used over the entire temperature range from -150°C to 2800°C. Generally, there may be four different furnaces used to cover this range: (a) -150 to 500°C, (b) 25 to 1000 or 1200°C, (c) 25 to 1600°C, and (d) 400 to 2800°C. The furnace may be positioned above, below, or parallel to the balance. Each configuration has its advantages and disadvantages; the furnace above the balance appears to be the preferred configuration for high temperature ranges, whereas for lower temperature, the furnace below the balance is more convenient. The rate of temperature increase or decrease is controlled by a furnace temperature programmer. this device should be capable of linear temparature programming. Heating of the furnace system should be linear with time and must be reproducible.

Most commonly used heating rates in thermogravimetry are linear, about 5-10°C min^{-1}. Faster heating rates are generally not employed unless very small samples are used or the investigation is a general survey of thermal properties.

As previously mentioned, in TGA the mass change of the sample is continuously recorded as a function of temperature. The temperature, in this definition, may be that of the furnace chamber, the temperature near the sample or the termperature of the sample. Schematic of TGA7 when using a standard furnace as shown in Fig. 2-5

The thermogravimetry analysis test procedures are as follow :

1)   Prepared solid sample by grinded, chopped or cut to small particles. Weight about 5-20 mg (depend on density of sample) and put into the cleaned sample pan, sample pan was cleaning either by using air/oxygen as a purge gas, heated TGA 950°C to burned off any residual material coated on the pan or by flaming the pan over a busen burner.

2)   TGA sample pan and the actual mass of materials is either electronically tared or subtracted by used of a computer software logarithm.

3) Set running conditions :

3.1 Temperature range   - Temperature start   50°C

- Temperature final   900°C

3.2 Heating rate   10°C/min.

3.3 Atmosphere   air

3.4 Flow rate   20 cm^3/min.

4) Run TGA as set condition and printed out the result from computer.

Fig. 2-5 Schematic of the TGA7 when using a standard furnace.
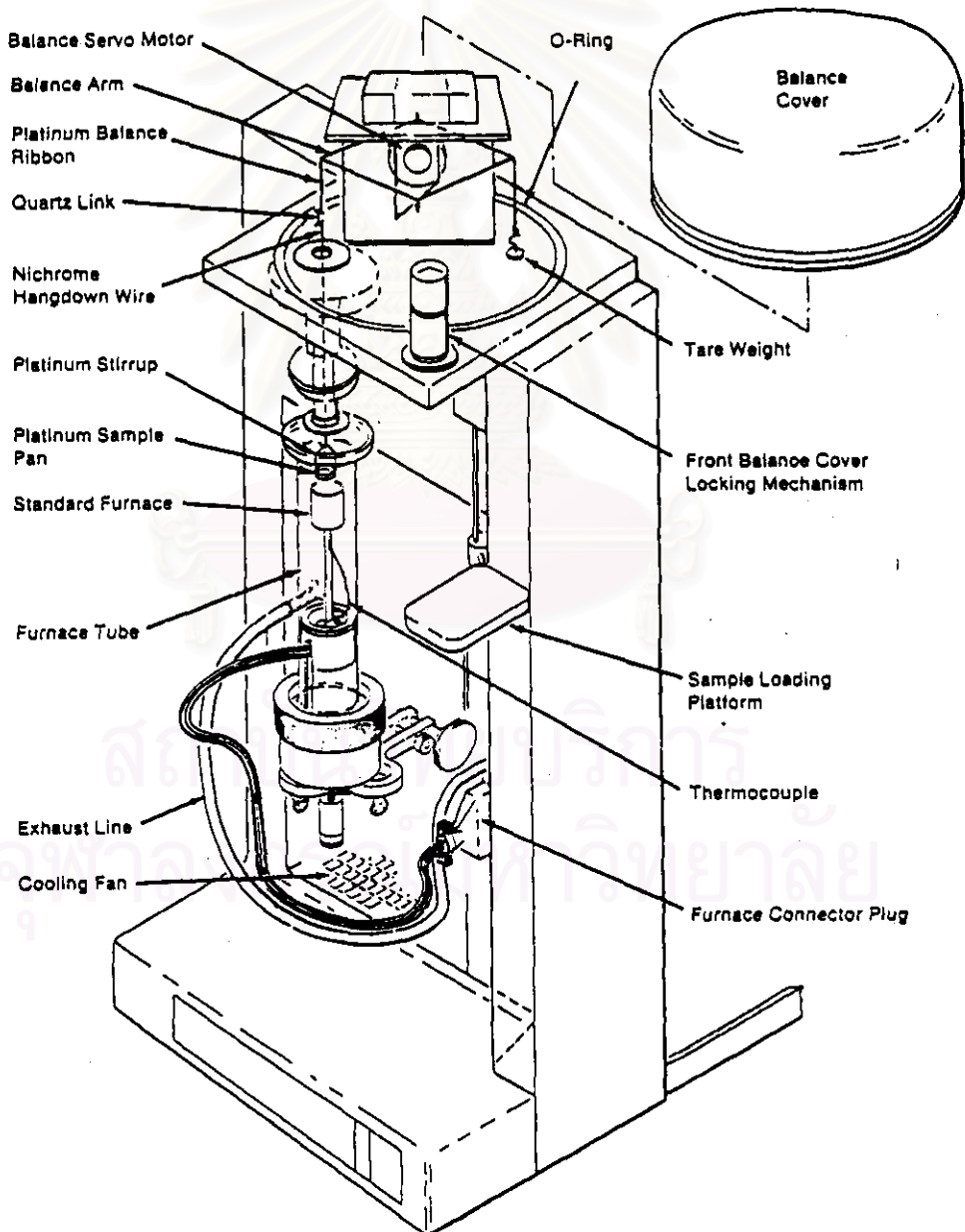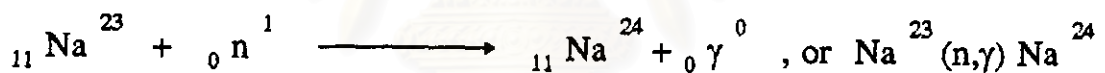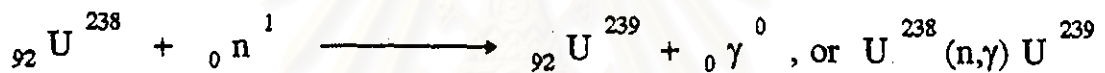
Neutron Activation Analysis (NAA)

Basic concepts of Neutron Activation Analysis (NAA) :

Activation analysis is commonly considered a method of analysis for chemical elements in trace quantities. A radioactive nuclide is formed when an element is bombarded by neutrons or charged particles such as electrons and protons etc.

A reaction used extensively in activation analysis is the (n,γ)-reaction, which is shown as examples in the following equations :

$$_{92}U^{238} + _{0}n^{1} \longrightarrow _{92}U^{239} + _{0}\gamma^{0} \text{ , or } U^{238}(n,\gamma)U^{239}$$

$$_{11}Na^{23} + _{0}n^{1} \longrightarrow _{11}Na^{24} + _{0}\gamma^{0} \text{ , or } Na^{23}(n,\gamma)Na^{24}$$

In a nuclear reactor, stationary conditions are established when the number of neutrons released in a given volume is about equal to the number of neutrons which participate in new fission acts. Neutrons from a nuclear reactor are composed of thermal and fast neutrons. Thermal neutrons are neutrons with an energy of about 0.025 eV.

The interactions between thermal neutrons and most of the nuclides through the (n,γ) reaction produce radioisotopes which can be identified by their characteristic decay rates and energies of the emitted radiations. The amount of radioisotope produced can be calculated from the well-known activation equation :

$$A \quad = \quad A_0 \, e^{-\lambda t} \qquad\qquad (2.1)$$

$$A_0 \quad = \quad A \, e^{\lambda t} \qquad\qquad (2.2)$$

from $\quad \lambda \quad = \quad 0.693 \, / \, T_{1/2} \qquad\qquad (2.3)$

$$A_0 \quad = \quad A \, e^{0.693 \, t \, / \, T1/2} \qquad\qquad (2.4)$$

where :

$A \quad = \quad$ Activity at time $= t$

$A_0 \quad = \quad$ Activity at time $t = 0$

$\lambda \quad = \quad$ Decay constat of product nuclide

$t \quad = \quad$ Decay time

$T_{1/2} \quad = \quad$ Half-life of product nuclide

Half-life $(T_{1/2})$ and decay time (t) must be the same unit of time. If the half-life of product nuclide is long when compared to decay time the term $e^{\lambda t}$ in equation (2-2) will approaches to 1.

Theoretically it is possible to calculate the amount of element present in a sample by comparing the count rate of a standard with that of the sample, one can determine the amount of each element in the sample by the following equation :
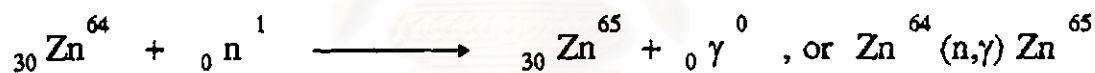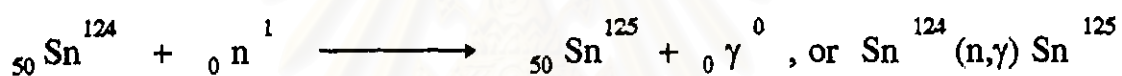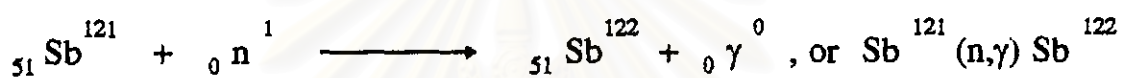
$$\% \, EX \quad = \quad \frac{C_{EX}}{C_{STD}} \quad x \quad \frac{W_{STD}}{W_{EX}} \quad x \quad \% \, STD \qquad\qquad (2.5)$$

where : $\quad \% \, EX \qquad = \qquad \%$ Element in sample

$\% \, STD \qquad = \qquad \%$ Element in standard

$$C_{EX} \quad = \quad \text{Count rate of sample}$$

$$C_{STD} \quad = \quad \text{Count rate of standard}$$

$$W_{EX} \quad = \quad \text{Weight of sample}$$

$$W_{STD} \quad = \quad \text{Weight of standard}$$

Reaction of element Sb, Sn, Zn when bombarded by neutrons shown in following equation :

$$_{51}Sb^{121} + _{0}n^{1} \longrightarrow _{51}Sb^{122} + _{0}\gamma^{0} \text{ , or } Sb^{121}(n,\gamma)Sb^{122}$$

$$_{50}Sn^{124} + _{0}n^{1} \longrightarrow _{50}Sn^{125} + _{0}\gamma^{0} \text{ , or } Sn^{124}(n,\gamma)Sn^{125}$$

$$_{30}Zn^{64} + _{0}n^{1} \longrightarrow _{30}Zn^{65} + _{0}\gamma^{0} \text{ , or } Zn^{64}(n,\gamma)Zn^{65}$$

Element Characteristic as follow :

Table 2-16 Characteristic of elemental.

Element	Molecular weight	Half-life	Energy (KeV)
Sb^{122}	121.75	2.7 days	564.1
Sn^{125}	118.71	9.5 mins.	332
Zn^{65}	65.39	243.8 days	1115.5

Kev = Kilo electron volt.

The neutron activation analysis test procedures are as follow :

a) Balanced the weight of sample inside polyethylene package "PE vial" before heat sealed it.

b) Balanced the calculated weight of elemental standard (that expected nearly to same amount elemental in sample) inside PE vial before heat sealed it.

c) Packed both vials of sample and standard in to polyethylene rabbit.

d) Irradiated sample pack c) with neutrons from nuclear reactor (as shown in Fig. 2-6) by loaded into load tube, loading time depend on each element, after that let it in shielding (protected irradiation) before counting activity rate.

Fig. 2-6 Nuclear reactor.

hidden
hidden
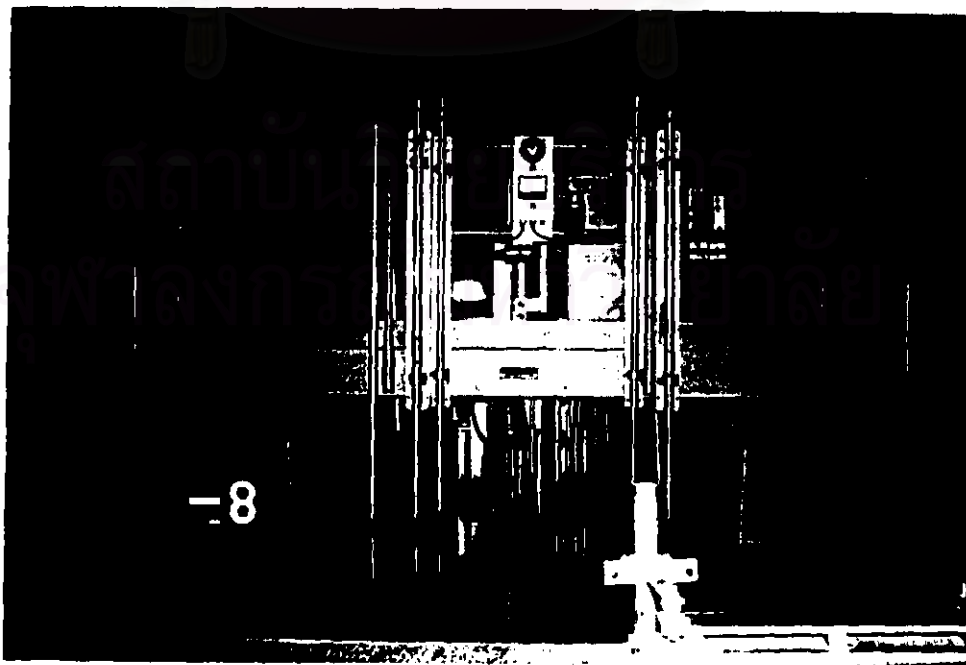
Loading time and decay period before counting activity rate.

element Sb loading time   1 hr.   decay period   24 hrs.

element Sn loading time   5 min.   decay period   10 min.

element Zn loading time   1 week   decay period   30 days

e)   Took all PE vials of sample and standard from rabbit and put each vial on the top of detector (as shown in Fig. 2-7) to detected count rate of each sample. Counting system diagram as shown in Fig. 2-8

f)   Calculated percentage of element in sample is shown in equation 3.5.

Fig. 2-7 Detector of NAA Canberra S100.

Fig. 2-8 Counting system diagram of neutron activation analysis.
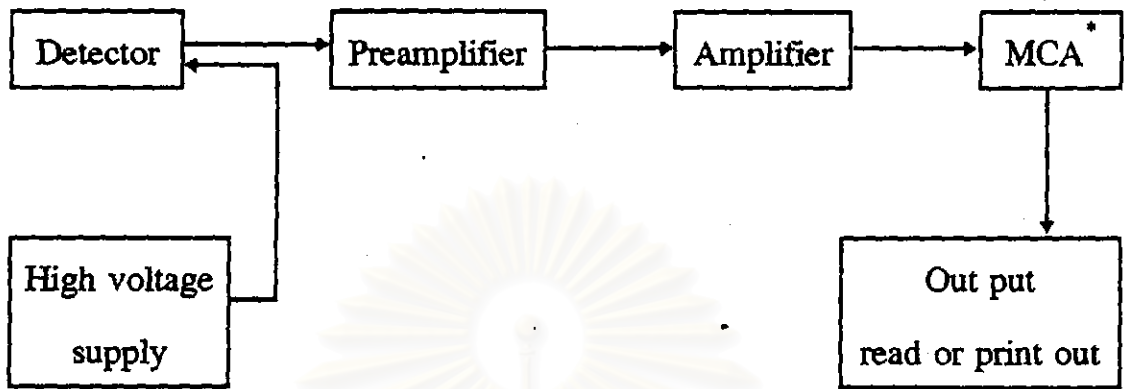
* MCA = Multichannal analyzer

Objective for thesis " Fire retarded mechanism of inorganic tin compounds in flexible poly (vinyl chloride) " is to study fire retarded mechanism of inorganic tin compounds zinc hydroxystannate and zinc stannate used as fire retardant in flexible poly (vinyl chloride).

Scope testings of this thesis after preparing specimens (by using a mechanical mixing machine to blend all ingredients and making testing sheets by two-roll mill) are :

1) Tensile strength, elongation at break and tearing strength tested by a tensile testing machine.

2) Detect percentage weight loss of sample by thermal analysis technic.

3) Use neutron activation analysis to consider quantity of elements in residue carbonaceous char.