DEVELOPMENT OF CADMIUM FREE LIQUID STABILIZER SYSTEMS FOR FLEXIBLE PVC

By

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURE

2-EHA	2- ethyl hexanoic acid
AOCS	American Oleochemical Society
ASTM	American Society for Testings and Materials
Ba	Barium
BaSt	Barium stearate
BC	Butyl cellosolve
β	Beta
C9	3,5,5-trimethyl hexanoic acid
Cd	Cadmium
DINP	Di-isononyl phatalate
DOA	Di-octyl adipate
DPM	Dipropylene glycol monomethyl ether
ESO	Epoxydized soybean oil
EDTA	Ethylenediamine-tetraacetic acid
EBT	Eriochrome Black T
eq	Equation
HCl	Hydrochloric acid
Hexamine	Hexamethylenetetramine
KCN	Potassium cyanide
K	Potassium
MW	Molecular weight
NH_3 35%	Ammonia
NH_4F	Ammonium fluoride
phr	Part per hundred parts of resin
Pb	Lead
RI	Refractive Index
TMP	Trimethylol propane
Zn	Zinc
ZnSt	Zinc stearate

PENGHASILAN SISTEM PENSTABIL CECAIR TANPA CADMIUM UNTUK PVC BOLEH LENTUR

ABSTRAK

Di dalam projek penyelidikan ini penstabil cecair tanpa pelarut telah dihasilkan daripada kalsium stearat dan zink stearat keluaran Stabilchem (M) Sdn. Bhd. Kalsium stearat dan zink stearat adalah diadunkan dengan pemplastik yang tak bertoksik, fosfat organik yang tak bertoksik dan juga antioksida yang tak bertoksik untuk menghasilkan penstabil cecair tanpa pelarut yang tak bertoksik. Kajian ini juga diperluaskan untuk menghasilkan sistem penstabil cecair di mana barium stearat dan zink stearat adalah penstabil utamanya. Penstabil cecair berdasarkan barium stearat dan zink stearat ini adalah untuk kegunaan dalam aplikasi yang tak ada kawalan ketoksikan. Pada tahun 1980-an, Housel telah berjaya menghasilkan penstabil cecair tanpa pelarut yang tak bertoksik terdiri daripada kalsium resinat, zink resinat, pemplastik, fosfat organik dan antioksida.

Sistem penstabil cecair tanpa pelarut jenis CaSt/ ZnSt yang nisbah logam Ca : Zn bernilai 1 : 1, 0.6 : 1 dan 0.3 : 1 menunjukkan kesan penstabilan (iaitu kemampuan mengekalkan kestabilan warna dan haba), sifat lutsinar dan pelinciran yang lebih baik daripada sistem penstabil cecair Ca/ Zn komersial iaitu NCE-94L dari Nan Ya. Bila dibandingkan dengan sistem penstabil cecair komersial jenis Ba/ Cd/ Zn iaitu LX-368N dari Nan Ya dan BC-310 dari Dansuk, didapati bahawa sistem penstabil cecair tanpa pelarut jenis CaSt/ ZnSt yang nisbah logam Ca : Zn dalam 0.3 : 1 adalah standing dengan kedua-dua jenis penstabil cecair komersial in dari segi sifat lutsinar dan

pelinciran tetapi kurang berkesan dari segi mengekalkan kestabilan warna dan haba. Sistem penstabil cecair tanpa pelarut jenis BaSt/ ZnSt yang mempunyai nisbah logam Ba : Zn dalam 4 : 1 jika dibandingkan dengan sistem penstabil cecair Ba/ Cd/ Zn, LX-368N dan BC-310 juga menujukkan sifat pelinciran yang lebih baik, kestabilan haba yang standing tetapi kurang berkesan dari segi mengekalkan warna. Kedua-dua jenis sistem penstabil cecair tanpa pelarut jenis CaSt/ ZnSt dan BaSt/ ZnSt adalah didapati standing dengan sistem penstabil cecair komersial jenis Ba/ Zn dari Nan Ya dan Dansuk.

Di dalam penyelidikan ini, dengan pemilihan sistem pelarut yang sesuai, garam Ba/ Zn telah berjaya dihasilkan dengan menindakbalas bersama barium hidroksida dan zink oksida dengan asid karboksilik dalam satu tindakbalas. Garam Ca/ Zn juga dapat dihasilkan dengan mengunakan cara tindakbalas yang sama. Garam Ba/ Zn atau Ca/ Zn ini kemudian diadunkan dengan fosfat organik, ESO dan antioksida untuk menghasilkan penstabil cecair jenis pelarut. Cara penyediaan penstabil cecair jenis pelarut yang dikemukakan dalam penyelidikan ini adalah lebih ringkas dan dipercayai dapat meningkatkan kesan penstabilan garam Ba/ Zn dan Ca/ Zn. Patent Amerika Syarikat 3,728,282 dan 4,401,779 telah menghasilkan penstabil cecair jenis pelarut dengan memperolehi terlebih dahulu garam barium, garam kalsium dan garam zink dari tindakbalas secara beasingan sebelum mengadunkan garam-garam logam ini bersama dengan fosfat organik, ESO dan antioksida. Jenis tindakbalas yang digunakan dalam kedua-dua Patent Amerika ini melibatkan lebih langkah tindakbalas.

Garam Ba/ Zn yang diperolehi dari tindakbalas barium hidroksida dan zinc oksida dengan campuran asid 3,5,5-trimetil heksanoik dan benzoik (dengan nisbah logam Ba : Zn dalam 3 : 1) dan garam Ca/ Zn yang diperolehi daripada tindakbalas kalsium hidroksida dan zink oksida dengan campuran asid 2-etil heksanoik dan benzoik (dengan nisbah logam Ca : Zn dalam 1.5 : 1) bila diadunkan bersama fosfat organik, ESO dan antioksida dapat menghasilkan penstabil cecair jenis pelarut yang setanding dengan penstabil cecair Ba/ Cd/ Zn komersial, malahan kesan penstabilannya juga lebih baik dari penstabil cecair komersial jenis Ba/ Zn dan Ca/ Zn.

Dari penyelidikan ini juga didapati bahawa kandungan fosfat organik dan ESO yang lebih tinggi dalam penstabil jenis bebas pelarut telah mengurangkan kebergantungan penstabil ini kepada Zn untuk mengekalkan warnanya. Kestabilan haba sistem jenis ini juga kurang dipengaruhi oleh kandungan Zn. Walau bagaimanapun, kalau membandingkan keberkesanan fosfat organik dan ESO dengan Zn berdasarkan berat yang sama, kedua-dua fosfat organik dan ESO adalah didapati kurang berkesan berbanding dengan Zn. Oleh itu fosfat organik dan ESO adalah kurang efektif dari segi kos berbanding dengan Zn untuk mengekalkan warna PVC.

ABSTRACT

In this research project, non toxic solvent free liquid stabilizers were developed based on calcium stearate and zinc stearate manufactured by Stabiichem (M) Sdn. Bhd. The metallic stearates used for the preparation of solvent free liquid stabilizers in this project were blended with non toxic plasticizer, non toxic antioxidant, non toxic phosphates and non toxic β-diketone to produce the non toxic solvent free liquid stabilizers. This preparation method has also been extended to produce the liquid stabilizer systems of which barium stearate and zinc stearate were the primary stabilizer for use in other than non toxic applications. In the 1980s, Housel has developed non toxic solvent free liquid stabilizer based on zinc resinate and calcium resinate, plasticizer, organic phosphite and antioxidant.

The developed solvent free liquid stabilizers based on CaSt/ ZnSt with a Ca to Zn ratio of 1 : 1, 0.6 : 1 and 0.3 : 1 displayed superior stabilizing effectiveness (i.e. initial color and heat stability), clarity and lubricity when compared to NCE-94L, a liquid Ca/ Zn system from Nan Ya. Comparison to commercial Ba/ Cd/ Zn system LX-368N from Nan Ya and BC-310 from Dansuk showed that solvent free liquid stabilizers based on CaSt/ ZnSt with a Ca to Zn ratio of 0.3 : 1 exhibited comparable clarity and lubricity but slightly inferior initial color and heat stability. Similarly, solvent free liquid stabilizers based on BaSt/ ZnSt with a Ba to Zn ratio of 4 : 1 displayed superior lubricity; comparable heat stability but inferior initial color and clarity when compared to commercial liquid Ba/ Cd/ Zn systems, BC-310 and LX-368N. However, the developed solvent free CaSt/ ZnSt as well as BaSt/ ZnSt liquid

stabilizers were equivalent to commercially available Ba/ Zn systems from Nan Ya and Dansuk.

In the development of solvent based liquid stabilizers, the Ba/ Zn salts of carboxylic acids or Ca/ Zn salts of carboxylic acids were successfully produced in a single step reaction with careful selection of the solvent system which acted as the reaction medium. The Ba/ Zn salts of carboxylic acids or Ca/ Zn salts of carboxylic acids obtained from reactions were blended with organic phosphites and other additives to prepare the solvent based liquid stabilizers. This method allowed a shorter reaction time and greater flexibility in adjusting relative amounts of Ba, Zn and Ca and the several carboxylate components. It was also believed that a more intimate mixture of the desired salts has also contributed to enhance stabilizing effectiveness. In United States Patent 3,728,282 and 4, 401, 779, the mixed metal salts were prepared by combining single metal salts that were obtained from separate reactions. The salt mixtures were then blended together with organic phosphite, acidic organic phosphate and hydrocarbon solvent to produce the solvent based liquid stabilizer formulations. Hence, solvent based liquid stabilizers produced according to these patents involved an additional reaction step as compared to the preparation method proposed in this research project. Solvent Based system developed in this research project which consist of Ba and Zn salt of 3,5,5-trimethyl hexanoic acid and benzoic acid mixtures with a Ba to Zn metal ratio of 3 : 1 and Ca and Zn salt of 2-ethyl hexanoic and benzoic acid with a Ca to Zn ratio of 1.5 : 1 were comparable to commercial Ba/ Cd/ Zn systems as well as superior to commercial Ba/ Zn and Ca/ Zn systems in initial color and dynamic heat stability.

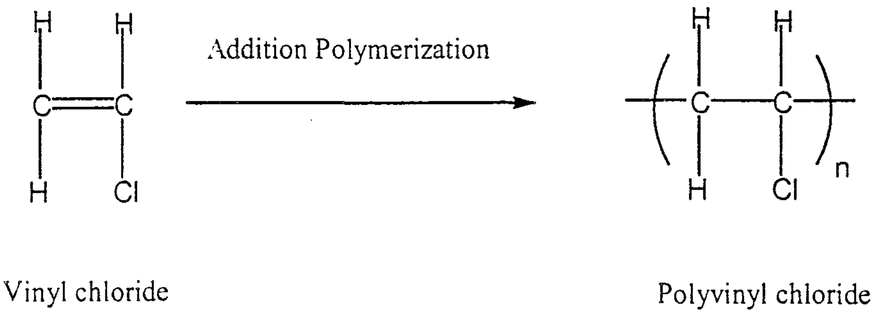
From this research project, it was also shown that higher content of organic phosphite and ESO in the developed solvent free stabilizers has reduced the dependency of the stabilizing systems on Zn to provide good initial color. And at the same time the heat stability of the PVC compound stabilized with these developed stabilizer systems will not be greatly affected by their Zn content. However, organic phosphite and ESO were found to be less effective as compared to Zn in the early color protection on a weight to weight basis. Therefore in general organic phosphite and ESO are less cost effective as compared to Zn in providing early color protection.

INTRODUCTION & LITERATURE SURVEY

1. INTRODUCTION & LITERATURE SURVEY

1.1 Introduction

Polyvinyl chloride or PVC resin is produced mainly by suspension (82 %), bulk (10 %) and emulsion (8 %) polymerization processes. All PVC is formed by addition polymerization of vinyl chloride as shown below.



In commercial resins, the degree of polymerization, n may have values between about 500 and 2000; i.e. the molecular weight range is roughly between 30,000 – 100,000 plus. PVC of much higher molecular weights has also been made (Penn, 1971).

PVC was developed by German chemist, Fritz Klatte in 1912 but it was not until 1926 that the American chemist Waldo Semon found the use in this polymer. PVC is useful because of its fire and water resistance. However, unlike most other plastics, PVC as sold in resinous form is unusable. Only by incorporating suitable additives e.g. stabilizers, lubricants, plasticizers, fillers, colorants, impact modifier, processing aid, blowing agent, etc. can the resin be converted to a form which can be processed into a useful end product. Depending on how it is formulated, it may be a rubbery flexible material or a rigid high impact product. It maybe opaque or crystal clear. It can be formulated to be nontoxic, nonflammable, light stable and stain resistant. Through proper formulation PVC has been used in such diverse applications as:

a) medical products e.g. blood bag, tubing, etc.
b) electrical and electronic products e.g. wire and cable
c) building and construction e.g. pipe, window siding, door, flooring, lighting etc.
d) toys
e) packaging e.g. bottles, closure liners and gaskets, coatings, film, sheets, etc.
f) consumer goods e.g. apparel, footwear, records, rain coat, shower curtain, luggage, umbrella, appliances, furniture, wall coverings, pail, etc.
g) transportation e.g. auto mats, auto tops, upholstery and seat covers

In worldwide commercial importance, PVC has become the second largest commodity plastic after polyethylene. World production of PVC resins in 1998 was estimated to be around 23.3 million tonnes of which 5.36 million tonnes was used in Western Europe. Most commodity plastics have carbon and hydrogen as their main component elements. PVC differs by containing chlorine (around 57 % by weight) as well as carbon and hydrogen. The presence of chlorine in the molecules makes PVC particularly versatile because chlorine makes it compatible with a wide range of other materials. The chlorine content also helps to make PVC flame retardant, therefore it is widely used for electrical insulation. Chlorine can also be used as 'marker' to distinguish PVC in automatic sorting systems for plastics recycling (Ramsay Plastics, 2001). Other reasons for acceptance of PVC include low ingredient cost, wide processing versatility, improve performance, increase decorative potential, etc (Wickson, 1993).

As this research project is on the development of liquid stabilizers for flexible PVC, the subsequent discussion will mainly focus on the stabilization of flexible PVC with liquid stabilizer systems.

1.2 Flexible PVC

PVC's mechanical properties can be adjusted over a wide range, yielding everything from rigid to flexible end products. It is possible to alter the stress-strain behavior of a plastic with additives called plasticizers. A plasticizer is a small molecule that makes plastics more flexible. For example, without plasticizers, PVC is a rigid plastic. Rigid unplasticized PVC is used for water pipes. But with plasticizers, PVC can be made flexible enough to make things like inflatable swimming pool toys. Flexible PVC also finds use in medical, automobile and packaging applications.

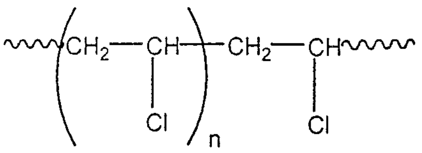
Flexible PVC has been an important synthetic alternative to natural rubber since 1940s. However, unlike rubber it has a tendency to discolor and is not easy to process well. Stabilization is required to perform two functions – to provide lubrication and to absorb hydrogen chloride (HCl) which evolves during processing. The lubricating function is important to provide metal release properties (i.e. to reduce adhesion of melt on equipment surface which will make processing difficult as well as promote early degradation due to greater heat transferred). In the meantime the evolution of HCl which takes place by elimination from the polymer backbone will result in the formation of conjugated polyene sequences and subsequently discoloration of the PVC formulation. Hence in the course of stabilizer development, the stabilizing effectiveness has been determined by the metal release properties as well as the quantity of HCl evolved or the extend of discoloration of the PVC formulations. Various metal soaps have been evaluated as stabilizers because they function as lubricants as well as absorbers of HCl. Some are better than others, while combinations of metal soaps have proved to perform better than single metal soap. Ultimately, barium and cadmium proved to be the most effective combinations and the term ` mixed metal stabilizer' was coined to refer to this type of products. As applications for flexible PVC grew, a number of ways of improving Ba/ Cd stabilizers have been examined (Barie *et al.*, 1973, Bae and Brecker, 1983, Bae *et al.*, 1988 and Aza *et al.*, 1989). These have included the addition of antioxidants, epoxy esters, polyols and phosphites – with each new ingredients improving stabilization. By the 1970s, many companies offered hundreds of products developed for specific applications that were still called mixed metal stabilizers, even though they contained many additional components. Since then environmental concerns and safety issues have become increasingly important. While the trend had previously been to add new components to Ba/ Cd stabilizers, they were now taken out. And in order to reduce volatile organic compounds, low boiling solvents that acted as compatibilizers for the liquid stabilizer solutions were removed. To reduce concerns about toxicity, Cd were replaced, particularly in flexible PVC applications such as medical tubing, refrigerator gaskets, flooring, wall coverings and swimming pool liners. This research program is therefore concentrated in the development of Cd free high boiling liquid stabilizers and their stabilizing effectiveness was being measured by the heat stability (i.e. discoloration and time to burn of PVC formulation) as well as the metal release properties (i.e. time to stick on equipment surface).

1.3 Degradation and Stabilization of PVC

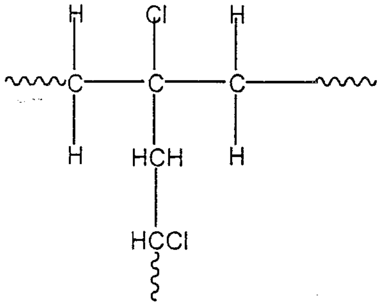
PVC is almost certainly the least naturally stable polymer in commercial use. It is known that PVC which is susceptible to degradation by heat and light would frequently undergo decomposition mainly caused by dehydrochlorination during thermal forming process or when used at a relatively high temperature environment or upon exposure to ultra-violet rays (Penn, 1971; Sugawara and Kobe, 1992). Thus attempts have been made to improve the stability of the PVC resin by adding several heat and/ or light stabilizers to the PVC resin. Therefore PVC has commercial acceptance on such a large scale is due principally to the successful development and application of effective means of stabilization. As the main focus of this research project is on heat stabilizers, the subsequent discussion will be based mainly on the thermal or heat degradation and stabilization of flexible PVC.

1.3.1 Degradation of PVC

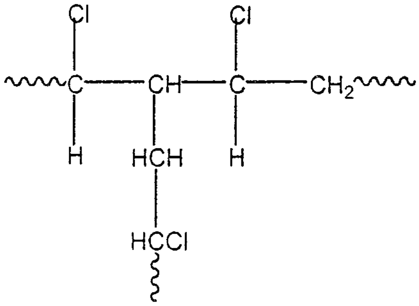
The instability of the PVC is linked to the structure of the polymer chains. Commercially prepared PVC does not correspond to any singular structure such as a regularly ordered repeating head to tail segmented chain as shown by eq [1], however, it can be viewed as a complex mixtures of many different entities, both straight chain and branched chain with a fairly broad molecular weight distribution (Nass, 1976). Branched structures e.g. as shown by eq [2] and [3] that occurred during the propagation of polymerization are believed to be present in commercially prepared PVC.



[1]



[2]



[3]

Other irregular group structures that are also found within PVC molecules that have been terminated by coupling include the followings:

$—CCl=CH_2$

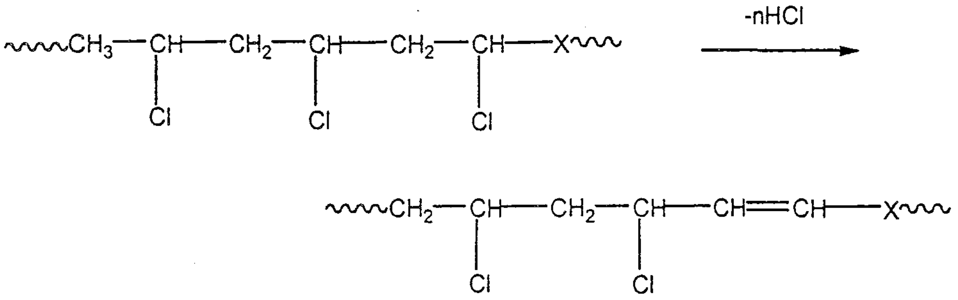
$—CH=CH_2$

$—CHCl-CH_3$

$—CHCl-CH_2Cl$

$—CH_2-CHCl_2$

If PVC in reality is corresponding to the idealized concept of regular repeating unit like eq [1], it would be expected to be a polymer of remarkable inherent stability. However, commercial PVC consists of the various groups illustrated earlier. And these different specific sites i.e. structural irregularities e.g. double bonds, tertiary chlorine, crosslinks, head to head sequences or conformational irregularities are considered to be degradation initiators. The main manifestations of degradation by heat are evolution of hydrogen chloride, discoloration or darkening, and deterioration in physical and chemical properties. All the above can be used to determine the stabilizing effectiveness of the stabilizer systems in a PVC formulation. Studies have shown that the weakness of the carbon-chloride bond is responsible for the initial degradation of PVC through the loss of hydrogen chloride at the irregular sites as in eq [4] (Chevassus and Broutelles, 1963; Nass, 1976; Wypych, 1986; Gachter and Muller, 1987; Mur and Madgwick, 1993).

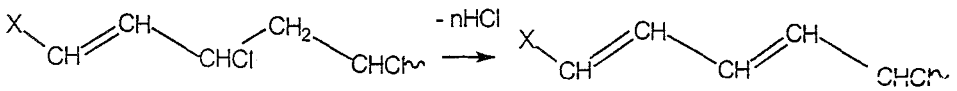


$$\sim\mathrm{CH_3}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{X}\sim \xrightarrow{-\mathrm{nHCl}} \sim\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH}=\mathrm{CH}-\mathrm{X}\sim \qquad [4]$$

Where X indicates the irregularities or activating group.

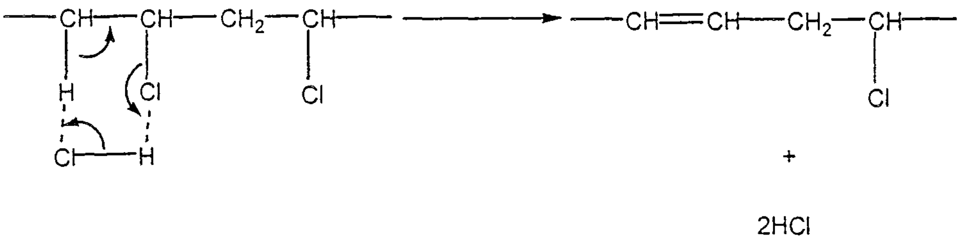
The elimination of the first molecule of hydrogen chloride and the subsequent formation of an unsaturated double bond on the PVC chain then activates the neighboring chlorine atom, which is now structurally located as an allylic chlorine. The allylic C-Cl bond energy is about 250 kJ/ mol while the regular C-Cl bond energy is roughly 300 kJ/ mol (Mur and Madgwick, 1993). The weakness of the allylic chloride bond leads to conjugated double bonds by the zip reaction as shown in [5].

This process will continue to repeat itself and proceeds quite rapidly, soon leading to a chain segment of polyunsaturation.



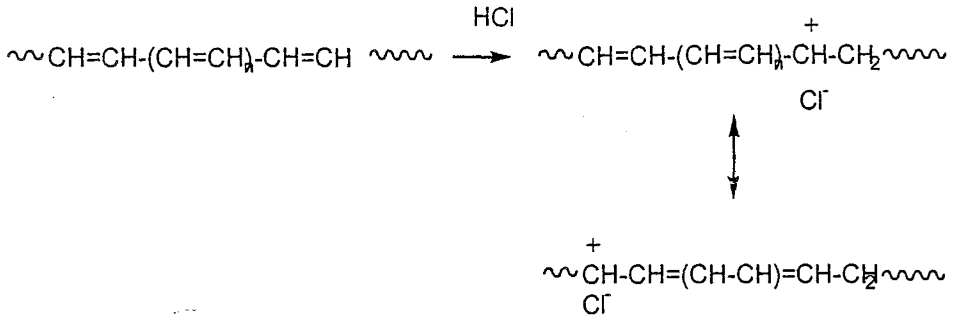
[5]

Both ionic and free radical mechanisms have been proposed to explain the progressive hydrogen chloride unzippering from a PVC chain, and the evidence collected to date shows that both processes maybe at work concurrently. Besides, HCl produced from unzippering of PVC chain is also shown to be able to catalyze the initiation of degradation through polarization of the PVC chain as illustrated in [6] (Wypych, 1986). This reaction will also lead to the formation of polyene sequences in PVC chains.



[6]

The polyene sequences with seven or more conjugated double bonds cause PVC discoloration. The basic property of polyenes is responsible for carbonium salts formation which enhances the discoloration effect (formation of carbonium salts is shown in reaction [7]).



$$\sim CH=CH-(CH=CH)_n-CH=CH \sim \xrightarrow{HCl} \sim CH=CH-(CH=CH)_n-\overset{+}{C}H-CH_2 \sim \quad Cl^- \; \updownarrow \; \sim \overset{+}{C}H-CH=(CH-CH)=CH-CH_2 \sim \quad Cl^-$$

[7]

Polyvinyl chloride is quite sensitive to even mild heating, and the formation of visible color usually is the first indication of degradation, chemical methods also indicate the evolution of hydrogen chloride. If heating is continued, physical changes will occur. Initially the polymer undergoes chain scission, leading to gradual degradation of mechanical properties and chemical resistance. This is soon accompanied by crosslinking, which in the later stages predominates. According to Druesedow (Mur and Madgwick, 1993; Benavides *et al.*,, 1996), crosslinking results from a Diels Alder reaction between polyene sequences. Rapid oxidation of polyene sequences also occurs, leading to formation of carbonyl and hydroperoxide groups. As these groups are formed, increase stiffening, insolubility and exudation of plasticizers (in the case of plasticized systems) are observed in PVC .

1.3.2 Stabilization of PVC

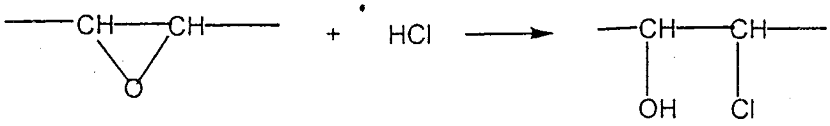
One of the most effective and widely used means of protecting PVC from thermal degradation is through the incorporation of thermal or heat stabilizers. This stabilizer system is a minor constituent of the total PVC composition and usually on the order of 0.5% - 3.0% of the system by weight. The effectiveness of heat stabilizers lies in their ability to hold and maintain the original color of a formulation, as well as holding and maintaining mechanical properties, chemical and electrical resistances, and so on. The 'ideal' stabilizer for PVC is considered to be a multifunctional material, or a mixture of materials capable of fulfilling the following roles:

a) Absorption and neutralization of hydrogen chloride evolved by the resin during and subsequent to processing of the composition.

Metallic salts of weak organic acids which are slightly basic react easily with hydrogen chloride and are converted to the corresponding metal chlorides (in eq [8] : M = metal, X= acid radical).

$$M(X)_n + nHCl \longrightarrow M(Cl)_n + nHX \qquad [8]$$

Other HCl acceptors are also used with a varying degree of success, such as epoxides in eq [9], amines in eq [10], metallic alkoxides and phenoxides in eq [11] and metallic mercaptides in eq [12].



$$-CH(-O-)CH- + HCl \longrightarrow -CH(OH)-CH(Cl)- \qquad [9]$$

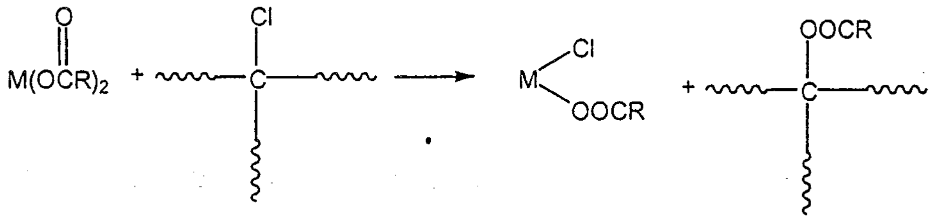
$$RNH_2 + HCl \longrightarrow RNH_3Cl \text{ (also secondary and tertiary amine)} \qquad [10]$$

$$R-O-M + HCl \longrightarrow MCl + R-O-H \qquad [11]$$

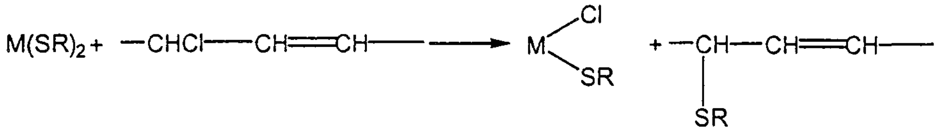
$$R-S-M + HCl \longrightarrow MCl + R-S-H \qquad [12]$$

b) Displacement of active, labile substituent groups, such as the chlorine atom attached to a tertiary carbon, or an allylic chlorine.

Among the most effective stabilizers are those that have been shown to function by actively attacking weakly held labile chlorine atoms on PVC and replacing these with other groups of inherently greater stability. The progressive zipper like dehydrochlorination is thereby thwarted before it commences by replacing the initiating, labile chlorine with other, more thermally stable groups that require higher energy levels before they are ruptured from the PVC chain. This is the Frye-Horst hypothesis which has gradually come to be the accepted mechanism by which the metal carboxylates and mercaptides function as color inhibiting stabilizers (Nass, 1976). The soaps of cadmium and zinc, and the dialkyl tin carboxylates and mercaptides, for example believed to stabilize PVC with mechanism as shown in eq [13] and [14].



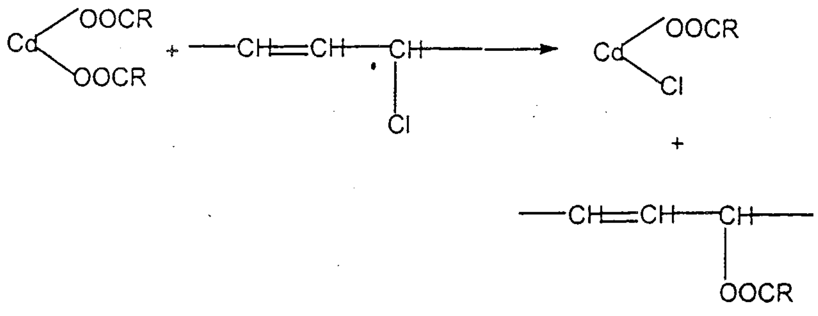
$$M(O\overset{O}{\overset{\|}{C}}R)_2 + \sim\sim\overset{Cl}{\overset{|}{\underset{\wr}{C}}}\sim\sim \longrightarrow M\begin{matrix}Cl\\OOCR\end{matrix} + \sim\sim\overset{OOCR}{\overset{|}{\underset{\wr}{C}}}\sim\sim \qquad [13]$$



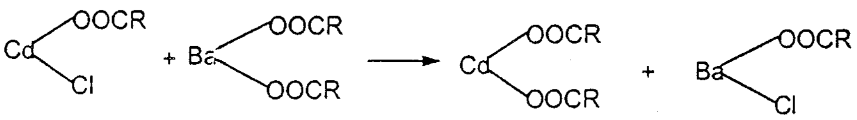
$$M(SR)_2 + -CHCl-CH{=}CH- \longrightarrow M\begin{matrix}Cl\\SR\end{matrix} + -\underset{SR}{\underset{|}{C}H}-CH{=}CH- \qquad [14]$$

c) Neutralization or inactivation of heavy metal chlorides which are the byproducts of stabilizers and could function as degradation initiator.

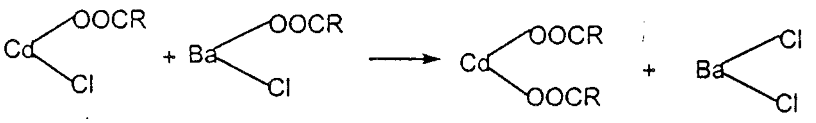
As the displacement reaction in [13] and [14] proceeds, the heavy metal chlorides e.g. cadmium chloride or zinc chloride that are formed are capable of initiating pronounced crosslinking and further hydrogen chloride evolution via the Friedel-Crafts type mechanism (Nass, 1976). Therefore some way to inhibit and deactivate the heavy metal chlorides is needed. In practice, we may use another material which may react with the newly formed metal chlorides immediately. This material may also functions by entering into the main reaction with heavy metal carboxylate (or mercaptide) at the time that the latter attacks the labile chlorine, at this point it accepts and thus deactivates the chlorine by preventing it from combining with the heavy metal. Alkali or alkaline earth metal carboxylates are preferred and the barium salts in particular are favored for this reaction. What probably takes place is the carboxylate of the alkali or alkaline earth metal regroups with the heavy metal cation. The active reagent necessary to stabilize the PVC is thereby regenerated, and the main reaction can continue without the immediate danger of stabilizer exhaustion or the formation of heavy metal chlorides (Lewis acid) that could function as alkylation catalysts. The sequence of reactions is illustrated in eq [15 – 17], in which the carboxylate soaps of Cd and Ba are used.



[15]

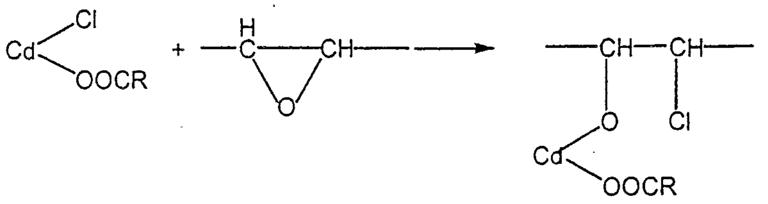


[16]

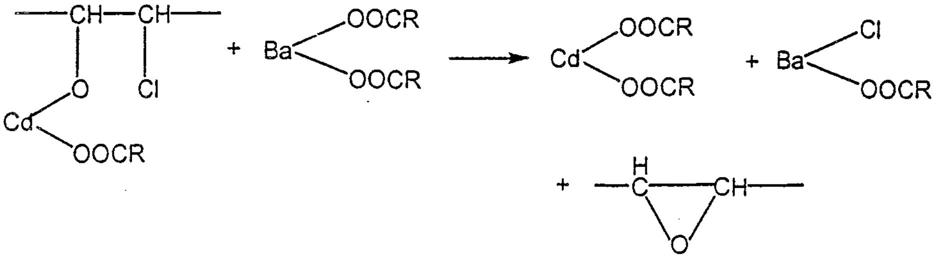


[17]

Another way of delaying the build up of heavy metal chlorides is by including the epoxides in conjunction with the heavy metal carboxylates and sometimes with the alkali or alkaline earth metal carboxylates also. Epoxides were believed to act as intermediate in transfer of the chlorine to the alkaline earth metal carboxylate as illustrated in eq [18] and [19] (Nass, 1976).



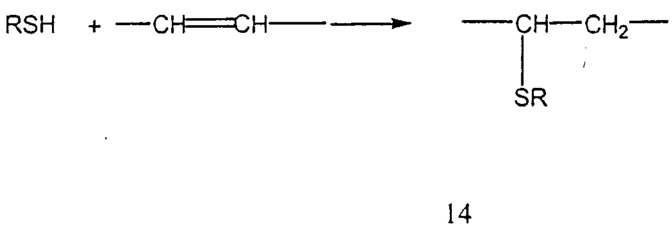
[18]



[19]

d) <u>Able to disrupt progression of unsaturation by e.g. addition reactions, free radical attack, reduction and oxidation.</u>

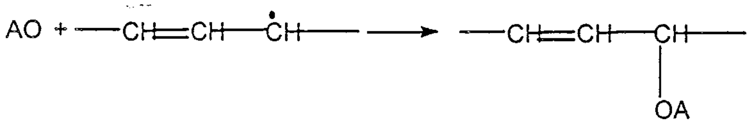
Mercaptans for example formed as an end product when metallic mercaptide stabilizers react with HCl as shown by eq [12], can subsequently add directly to double bonds to form thioether groups according to reaction [20]. When a polyene sequence is broken up in this manner, the color of the polymeric consequently reduced as well.



$$\mathrm{RSH} + -\mathrm{CH}{=}\mathrm{CH}- \longrightarrow -\underset{\displaystyle \mathrm{SR}}{\mathrm{CH}}-\mathrm{CH_2}- \qquad [20]$$

e) The termination of the of a typical free radical oxidative sequence by an antioxidant radical.

The termination of the of a typical free radical oxidative sequence by an antioxidant radical illustrated in eq [21] is yet another addition mechanism that is believed to be important in the overall stabilization scheme of a complex stabilizer mixture.



[21]

f) Neutralization or inactivation of resin impurities, contaminants, catalyst residues, end groups, etc.

The two mechanisms most often cited are chelation and antioxidation (free radical quenching) e.g. by tertiary phosphites.

1.4 Classification of Stabilizer Systems for PVC

There are many different schools of thought on how to classify the stabilizing systems of PVC, namely

(1) according to the physical form of the commercially available stabilizer systems, they are mainly found as:

a) Solid type stabilizers and

b) Liquid type stabilizers.

(2) according to the function of the various stabilizer systems available, the stabilizer systems can be broken down into three main groups as follows:

a) Lead salts which are mainly found in solid form,

b) Organotin compounds in both solid and liquid forms and

c) Combination of mixed metal salts and co-stabilizer systems in both solid and liquid forms.

(3) according to the formulations of PVC compounds e.g. plasticized/ non plasticized PVC formulations, PVC plastisol formulations or toxic/ non toxic PVC formulations.

Liquid stabilizer are widely used in the plasticized PVC formulations and due to the requirement to maintain certain rigidity in the rigid PVC compound, solid stabilizers are mainly used in the non plasticized PVC formulations. Liquid Ba/ Zn, Ca/ Zn and organotin systems are most widely used as stabilizers for plastisol processing whereas due to its toxicity Cd containing stabilizers are only used to a very limited extent in plastisol processing. PVC formulations for food and blood contact do not allow the use of Ba based, Cd based, lead based or dibutyltin stabilizer systems.

1.4.1 Lead Salts or Soaps

Lead compounds are now used principally in stabilizing plasticized PVC for electrical wire and insulation as well as rigid PVC compounds for certain piping and electrical conduits. Example of lead salts used for the stabilization of PVC is tribasic lead sulfate, dibasic lead phtalate, dibasic lead phosphite, normal lead stearate, etc. Little is known on how lead stabilizer functions except for their acid-accepting ability and that the chlorides of lead are insoluble and nonionizable. As they are not ionic and do not conduct electric, these accounts for their great use in electrical insulating materials. Since the lead chloride by product is incapable of initiating further degradation, this probably explains why the lead salts can be used alone. Among the advantages to be gained through the use of lead stabilizers are a relatively low cost per pound, a degree of light stabilization that is unsurpassed by other metallic derivatives as well as the absence of problems such as stabilizer volatility, plastisol viscosity build up and reduction in the heat distortion temperature of rigid compounds. In vinyl foam formulations, basic lead salts are also effective promoters or catalysts for the decomposition reaction of azodicarbamide (blowing agent), this making expansion possible at low temperatures. However, lead stabilizers are not acceptable stabilizers when clarity is a prime requisite. Furthermore all lead stabilized vinyl compositions are prone to sulfide staining when exposed to industrial atmospheres rich in hydrogen sulfide fumes. Other drawbacks to lead stabilizers are associated with the toxicological characteristics of lead salts, difficulty in handling due to their propensity towards dusting as majority of lead stabilizers are in solid form, as well as the fact that efficient lead stabilization requires a higher concentration of additive than is the case with other stabilizing materials, mostly on the order of 5 – 8 parts per hundred of resin. Some of the commercially available lead stabilizers are e.g. SAK-TS, a tribasic lead sulfate from Sun Ace Kakoh, Japan (Sun Ace Kakoh, 1991); Barostab V420 MC, a tribasic lead sulfate and Barostab Pb51 S, a dibasic lead stearate from Baerlocher, Germany (Baerlocher Additives, 1995).

1.4.2 Organotin Compounds

The organotin stabilizers are normally compounds of either dibutyl tin or dioctyl tin with various organic materials such as certain fatty acids (frequently lauric and maleic) and thio compounds e.g. mercapto acids. The group includes both liquid and solid stabilizers.

Regardless of the particular alkyl groups of the organotin compounds, the overall performance of organotin stabilizers, as a group, comes closer to the hypothetical 'ideal' stabilizers than any other of the widely used metallic combinations. It was postulated that organotin salts could neutralize HCl evolved by the resin as shown in eq [12], but it was also shown in eq [14] that organotin could function by donating their anionic ligands in a direct replacement of labile chlorines on the PVC chain.

It was found that no matter which reactions predominates i.e. hydrogen chloride neutralization or labile chlorine displacement, the by product, dialkyltin dichloride, a relatively weak Lewis acid as compared to heavy metal chlorides, does not initiate further degradation of the PVC. And reaction [14] was believed to account for the color holding ability and the maintenance of melt rheology that the stabilizer contributes. Most organotin stabilizers and their by products are completely soluble in PVC and most plasticizers. Organotin stabilizers therefore impart a degree of clarity unsurpassed by any other metallic stabilizer systems, the initial clarity being unaffected by the extent or severity of processing. In addition, neither the organotin stabilizers nor their by products exhibit any tendency to water blush or fog when clear PVC are exposed to moisture and humidity for long periods. The nonpolymeric organotin have proved to be the most versatile type of stabilizer for rigid PVC processing.

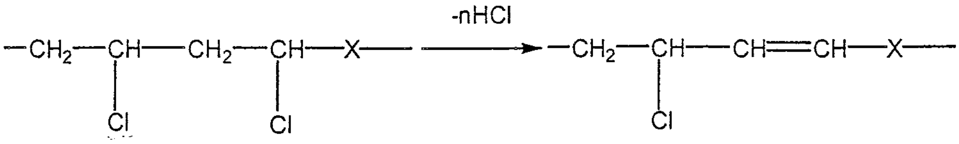
One interesting characteristics of the organotin stabilizers is they are not benefited in performance with the use of co-stabilizers e.g. epoxide, tertiary phosphite and polyhydric alcohols normally used in other metallic compounds (except lead).

In overall heat stability, it is generally agreed that the alkyltin carboxylates are not as efficient color inhibitors as good Ba-Cd-Zn-epoxide-phosphite-phenol mixed system. Typical organotin stabilizers are not highly dipolar and therefore are not effective lubricants. The compound stabilized with organotin stabilizers has a tendency to stick on the processing equipment, calcium or barium stearate are normally employed as the lubricant. Sulfur cross-staining of lead compounds can also occur with tin mercaptides. The chief commercial drawback to all organotins, regardless of structure, is that they are still considerably more expensive to manufacture than stabilizers based on lead salts or the mixed-metal combinations. Organotin stabilizers are approximately three to four times as expensive as the average Ba/ Zn system and about five times as costly as the average lead stabilizer on a same weight basis. Example of some commercially available organotin compounds are Thermolite 831, a non toxic octyltin mercaptoacetate for calendered sheet from Elf Atochem and StanclereT-233P, an estertin mercaptoacetate for rigid PVC formulation from Akzo Chemicals (Wickson, 1993)

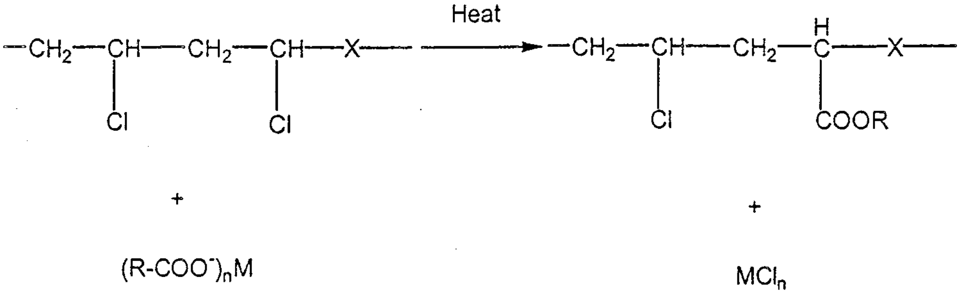
1.4.3 Mixed Metal Salts or Soaps

The metal salts of organic acids are also known as metal soaps (Szczepanek, 1970; Wypych, 1986). In this case the metal is for example cadmium, (Cd), calcium, (Ca), barium, (Ba), zinc, (Zn) and much less commonly also sodium, (Na), potassium, (K), magnesium, (Mg), and aluminium, (Al) (Chevassus and Broutelles, 1963; Penn, 1971; Nass, 1976; Wypych, 1986; Wickson, 1993). The organic acids can be from saturated or unsaturated linear aliphatic carboxylic acids, aromatic carboxylic acids or branch chain aliphatic acid or a combination of all the above. (Barie *et al*, 1973; Rhodes et al, 1973; Rhodes et al, 1975; Housel, 1982; Minagawa and Nakahara, 1991; Bae and Brecker, 1983; Aza *et al.*, 1989; Sander *et al*, 1994; Tadenuma *et al.*, 1991; Sugawara and Kobe, 1992; Anderson, 1996; Croce *et al.*, 1999).

The stabilization mechanism of metal soaps has been reported in many literatures (Chevassus and Broutelles, 1963; Nass, 1976; Wypych, 1986; Benavides *et al.*, 1996; Gokcel *et al.*, 1999). The carboxylate group of the metal soap substitutes the tertiary or allylic chlorine atoms and stops the initiation of dehydrochlorination according to the well known Frye and Horst mechanism. The parallel reactions that occur during dehydrochlorination of PVC in the presence of metal soaps are:



$$-CH_2-\underset{\displaystyle Cl}{CH}-CH_2-\underset{\displaystyle Cl}{CH}-X- \xrightarrow{-nHCl} -CH_2-\underset{\displaystyle Cl}{CH}-CH=CH-X- \quad [22]$$



$$-CH_2-\underset{\displaystyle Cl}{CH}-CH_2-\underset{\displaystyle Cl}{CH}-X- + (R\text{-}COO^-)_nM \xrightarrow{Heat} -CH_2-\underset{\displaystyle Cl}{CH}-CH_2-\underset{\displaystyle COOR}{\overset{\displaystyle H}{C}}-X- + MCl_n \quad [23]$$

$$(R\text{-}COO^-)_nM + nHCl \longrightarrow nR\text{-}COOH + MCl_n \quad [24]$$

Where X represents an activating group such as >C=O, -C=C-, etc. The rate of reaction [22] is accelarated by HCl and MCl_n which are products of reaction [22] and [23] respectively. HCl can be removed from the medium by reaction [24], with formation of more MCl_n which may be a Lewis acid, accelerating reaction [22]. Thus by employing a second metal soap as in the mixed metal soaps systems, it will react with MCl_n to give a salt M_1Cl_{n1} without acidic properties as illustrated in reaction [25].

$$n(R\text{-}COO^-)_{n1}M_1 + n_1MCl_n \longrightarrow n_1(R\text{-}COO^-)_nM + nM_1Cl_{n1} \quad [25]$$

The mixtures of metal soaps where M is either zinc or cadmium and M_1 is either barium or calcium are extensively used stabilizer systems. Wypych, 1986, has also shown that in the presence of only barium soaps, polyene sequences grow from the beginning of a heat test, therefore barium soaps gave poor early protection, however, as barium chloride formed during the displacement of labile chlorine is a weak Lewis acid and quite stable chloride, it provides good longer term stability. In another instances when only zinc soaps were applied, at initial stages polyene sequences remain stable in length, zinc carboxylate are highly active in compositions of broad solubility parameter and readily permeate plasticized composition leading to excellent early protection by temporarily stopping the zip effect. Following this model zinc soaps prevent color development. But zinc chloride or zinc chlorohydric acid are strong Lewis acids and consequently can promote dehydrochlorination or degradation after its concentration builds up to a certain point, hence the rapid growth in polyene sequences at the later stage. Cadmium soaps were found to behave the same as zinc soaps and calcium soaps perform in a manner similar to that of barium soaps. Hence the mixtures of metal soaps has a better stabilizing effect than the single metal soap (Barie *et al*, 1973; Rhodes et al, 1973; Rhodes et al, 1975; Housel, 1982; Minagawa and Nakahara, 1991; Bae and Brecker, 1983; Aza *et al.*, 1989; Sander *et al*, 1994; Tadenuma *et al.*, 1991; Sugawara and Kobe, 1992; Anderson, 1996; Croce *et al.*, 1999).

Mixed metal soaps which consist mostly of combinations of two or more metal organic salts plus certain organic co-stabilizers, rank in the number one position both in volume of stabilizer used and in diversity of formulations and applications in which they appear. They are the most versatile group of stabilizers available, since they are so amenable to custom formulation. The mixed metal soaps are available as a one pack stabilizer in liquid, solid form or to a lesser extent in paste form; or they may be purchased as separate components and introduced into the vinyl compound in different ratios.

It is general practice to refer to the various mixed metal salts as the 'primary' stabilizers, since these by themselves will convey a moderate degree of stabilization efficacy when blended with PVC. However, they are numerous organic compounds that may be used in conjunction with these mixed metal salts to enhance its stabilizing effectiveness (Nass, 1976 and Wypych, 1986). By themselves, or in combinations with each other, these organics are not particularly effective as PVC stabilizers. They are mainly used as co-stabilizers, to enhance further the overall stabilization performance of the mixed metal systems. These organic adjuvants or co-stabilizers include β-diketone, tertiary phosphites, epoxides, polyhydric alcohols, phenolic antioxidants, etc.

1.4.3.1 Barium-Cadmium and Barium-Cadmium-Zinc Systems

Of all the mixed metal systems, those based on Ba and Cd salts or Ba, Cd, and Zn salts are used in the largest volume and in widest variety of circumstances. However due to the gradual awareness and increasing concern over toxicological consequences associated with the use of Cd and its salts, there is both a growing public pressure and a steadily rising resistance from industry towards using stabilizers containing Cd.

The Ba/ Cd systems are mainly solid stabilizers whereas the Ba/ Cd/ Zn systems are largely found in liquid forms. In these stabilizer systems are normally incorporated co-stabilizers like phosphites, epoxy compound or UV absorbers for out door applications.

For high clarity products of good early color, high Cd is found in the stabilizer systems, while for long term stability, the amount of Ba is considerably increased. Additionally the increase in Zn is meant to deter sulfide staining. Mixed metal stabilizers of this group is known for good efficiency and long term stability, and due to the presence of Cd stabilizer they also give light fastness to final products. Their ability to form transparent plasticates is one of their essential features. Their main disadvantage though is the toxicity of the Cd metal, the propensity of PVC to sulfide staining when a Cd stabilizer is used and in the case of solid Ba/ Cd stabilizers is the tendency to `plate-out' (Jae and Drexler, 1984 and Wypych, 1986). Some commercially available Ba/ Cd/ Zn systems are e.g. Chemstab MAE, a liquid Ba/ Cd/ Zn stabilizer for extrusion of flexible PVC compounds and plastisols from EastPoint Chemicals (EastPoint Chemicals, 1996); Barostab 361, a solid Ba/ Cd/ Zn stabilizer for filled calendered products from Baerlocher (Baerlocher additives, 1995) and V-1277, a solid Ba/ Cd stabilizer from BASF (Wickson, 1993).

1.4.3.2 Barium-Zinc Systems

Ba/ Zn soaps are sufficiently effective to be used as general purpose stabilizers from plastisols to rigid products. Ba/ Zn stabilizers are produced in both solid and liquid form and normally include an epoxydized oil, β-diketone and phosphite compound.

Baker, 1990 and Wickson, 1993 have reported formulations based on a Ba/ Zn metal ratio of 4 : 1. Recently Croce *et al.*, has also evaluated weight ratio of barium to zinc in the range from 2 : 1 to 6 : 1 and found that a ratio of 4 : 1 was most preferred. Baker, 1990 has reported that Ba/ Zn formulations with Ba/ Zn/ dibenzoyl methane weight ratio of 4 : 1 : 1 were comparable to Ba/ Cd/ Zn stabilizers; the wt % of Ba and Zn used was 5 % and 1.2 % respectively.

PVC compound stabilized with Ba/ Zn systems are normally free from sulfide staining. However, Ba containing stabilizers can not be used in contact with food products. Ba/ Zn stabilizers impart quite good heat resistance but not very good resistance to light. Some commercial examples of Ba/ Zn stabilizers are BZ-380A, a liquid Ba/ Zn stabilizer from for flexible transparent and colored expanded leather film and sheet from Dansuk (Dansuk Information, 1995); Lox-3K-8T, a liquid Ba/ Zn stabilizer for flexible and semirigid PVC products by calendering or extrusion from Nan Ya (Nan Ya Stabilizers, 1995) and UBZ 637, a liquid Ba/ Zn stabilizer for transparent and white pigmented applications from Baerlocher (Baerlocher Additives, 1995).

1.4.3.3 Calcium-Zinc Systems

Stabilizers in this group have a full variety of applications for the processing of rigid, semi-rigid, and plastisols, but their main advantage is their low toxicity, which allows them to be used in products in contact with food and pharmaceuticals, and also in PVC materials applicable in medicine. These stabilizers are divided into two classes, low toxic and non-toxic and the main difference between them is the type of fatty acids used. Low toxic stabilizers contain lower fatty acids, including C_{15} whereas non toxic stabilizers are normally produced from stearic acid. These Ca containing systems have reasonable stability to heat and light.