The process of recommending an optimum stabilizer for a particular vinyl application, then selecting and evaluating that stabilizer, can be a formidable task. This is especially due to the vast numbers of stabilizers which are marketed to the PVC industry world-wide. There are many well regarded stabilizer producers in North America, Europe, and the Far East, as well as many more producers in Latin America and India. Most of these offer many commercially available stabilizers in their product lines, some in the dozens!

One reason so many stabilizers are offered to vinyl compounders is that the PVC compounding industry has become more astute and sophisticated over the years, requiring development of stabilizers to fill many specific requirements other than simply to provide process heat stability for PVC compounds.

Another reason for the large selection of stabilizers centers on the wide diversity of vinyl applications and methods of processing. PVC is truly the most versatile of all polymers! The total “Heat/Shear History” of vinyl compounds can vary significantly in both amount and type among different applications. This concept of “Heat History” and The total capacity of the stabilizer system to furnish the required protection is perhaps an over-simplified way of integrating the total energy input of all types to which a vinyl compound is subjected over a product’s useful life span.

The shear and heat energy of mixing cycles (dryblend, banbury, high speed plastisol dispersators), processing (calender, extruder, molder), fabricating (embossing, thermoforming, laminating ), scrap re-work, heat and light energy of outdoor exposure, heat of a product’s use environment (auto interior, hot air duct) , Gamma ray sterilization, and other end-use requirements-- all contribute to overall PVC degradation. The stabilizer system must be able to furnish adequate protection at every stage during the production and useful service life of the vinyl product. The amount and type of energy input varies considerably among the many different production methods and end-use applications of PVC. Also, the accumulated storage history of PVC resins before compounding can vary. Resin degradation actually starts in the polymerization reactor and can continue under storage conditions through oxidation, carbonyl formation, etc. even before use.

The purpose of this discussion is to present a logical sequence of factors to consider in selecting a stabilizer, in order to provide a practical means first to select a generic group or class of stabilizers, and secondly to choose a specific stabilizer within the class to fully optimize the selection. Theoretical discussion of PVC stabilization and chemical mechanisms offered to explain the hows and whys of stabilizer behavior will not be presented in this treatise.
GENERAL STABILIZER GROUPS

There are several basic groups of heat and light stabilizers currently offered to the vinyl industry:

1) Mixed metal-organic acid salts (liquid and solid), consisting of any one or a combination of Barium, Calcium, Cadmium (disappearing), and Zinc. Typically, C8 to C18 straight chain or branched chain aliphatic carboxylic acids are used. Aromatic (alkyl benzoic) acids once used are no longer in favor due to toxicity concerns.

2) Organotin compounds (liquid and solid), mainly mercaptoester and mercapto alcohol types (sulfur-containing), and carboxylate or dicarboxylate (non-sulfur) ester types.

3) Lead salts and soaps (liquid and solid)

4) Calcium-Zinc carboxylate packages (liquid, paste, powder) containing USFDA/BGA sanctioned ingredients for “nontoxic” applications.

5) Organic and miscellaneous types, including alkyl/aryl phosphites, epoxy compounds, beta-diketones, amino crotonates, nitrogen heterocyclic compounds, organosulfur compounds (i.e. ester thiols), hindered phenolics, and polyols (pentaerythritols). These types currently are being heavily researched, and their use at the expense of metal-containing stabilizers is expected to grow significantly.

6) A minor group consisting of carboxylic or mercaptoester salts of antimony, strontium, potassium.

Generally speaking, flexible vinyl compounds which are calendered, extruded, or molded and plastisol compounds most commonly are stabilized with (1) the mixed metal Ba/Zn, Ca/Zn systems. Applications requiring USFDA or BGA sanction for direct or indirect food contact and most medical applications utilize the (4) “non-toxic” Ca/Zn systems.

Rigid vinyl compounds for extrusion and molding are stabilized most frequently with (2) organotin mercaptides in North and South America, and parts of the Far East, and (3) Lead or (1) Mixed Metal systems in Europe.

Flexible vinyl compounds used in electrical wire coating applications are mostly (3) Lead stabilized, since leads offer the best electrical properties - due primarily to the insolubility of lead chlorides formed during stabilization. Currently lead is under pressure for possible replacement by special mixed metal systems, in secondary and decorative wire insulation. However, primary insulation is still best stabilized by lead.
FACTORS GOVERNING OPTIMUM STABILIZER SELECTION

The factors to consider in making an optimum stabilizer selection for a given vinyl process can be divided into three broad categories:

- **Formulation Variables**
- **Process Variables**
- **End-use Properties**

**Formulation variables** such as PVC resin, impact modifying resins, processing aids, plasticizers, fillers, pigments, lubricants, foaming agents, and other miscellaneous ingredients can all have an effect upon or be affected by the stabilizer.

**Process Variables** which can be a determinant in stabilizer selection include consideration of compounding procedures (Banbury, Dryblend, Plastisol Mixing), calendering, extrusion (single or twin screw), injection molding, blow molding, coating molding or dipping of plastisols and organosols, solution vinyl systems, foamed vinyls and fluidized bed powder coating. Other considerations of processing include melt rheology, plastisol viscosity properties, plate-out, scrap re-work, etc.

**End Use Properties** that affect stabilizer selection include clarity, outdoor weathering, toxicity, stain resistance (sulfide, urethane, asphalt), impact strength, heat distortion, electrical properties, odor, effects of moisture (haze, dimensional stability), heat-sealing and printability, and “fogging” (automotive and food wrap film).

**FORMULATION VARIABLES**:

**Vinyl Resins** - The wide variety of differing types of PVC resins which require stabilization, and the large number of resins available within each variety probably is the single greatest factor which explains the large number of commercially available stabilizers confronting the vinyl compounder. PVC homopolymer is produced by suspension, bulk (or mass), and emulsion polymerization methods. The amount and type of residual components on the resin shipped to users (catalyst residues, suspension agents, emulsifying agents, etc.) can differ to the extent that even vinyl resins manufactured by the same polymerization method from different producers can vary in their response to a given stabilizer system. Moreover, since the Vinyl Chloride Monomer crisis of the early 1970’s, efforts to reduce residual VCM by steam-stripping and more rigorous drying procedures added another dimension to resin variability since no two producers’ techniques were identical. “Pink”, or off-white PVC sometimes found its way to customers--- especially during tight supply periods!
Post-chlorinated PVC (High Temp.), with a very narrow processing window offers additional stabilization challenges.

Vinyl acetate- vinyl chloride copolymers and vinyl chloride with other co-monomers (propylene, cetyl vinyl ether, vinylidene chloride) also differ widely in their response to a given stabilizer system. One of the most striking differences in stabilizer response occurs with mixed metal Ba/Zn, Ca/Zn, and (formerly) Ba/Cd/Zn stabilized formulations. This phenomenon is known as “Zinc Sensitivity”, and is seen as a drastic discoloration- even burning- in PVC compounds subjected to progressive exposure to heat. PVC resins can vary considerably in their response to varying zinc levels of a stabilizer system. Years ago, most then commercially available vinyl resins were classified as to “Zinc Sensitivity”, in addition to the ASTM D-1755-60T (1960) cell classification covering other resin properties. This classification unfortunately has fallen by the wayside over the ensuing years, but is still a viable tool for the astute compounder.

In the figures, “Zinc Sensitivity”, we see the different response of four PVC resins, each stabilized with a series of three Ba/Cd systems differing only in the level of Zn, and exposed in an oven at 350 deg.F for an increasing number of 10 minute intervals.
PVC resin A exhibits slight improvement as the zinc content is increased, and we see that the presence of zinc in the stabilizing system for this resin is beneficial. The stability of resin B is neither enhanced nor materially retarded with increasing levels of zinc. Stability of resin C is moderately affected by increasing zinc levels of the stabilizer system, while resin D is extremely sensitive to the presence of even small quantities of zinc. Many vinyl acetate/vinyl chloride copolymers are extremely zinc sensitive and would be comparable to resin D. In fact, the zinc sensitivity of a vinyl acetate/vinyl chloride copolymer is directly proportional to the vinyl acetate content of the copolymer.

A word should be said at this point about the contribution to stability of the various components in a mixed metal stabilizer system. Our example is a Ba/Cd/Zn system, although cadmium is no longer used by most. As can be seen in the figure, “Effect of Stabilizer Components”, the barium component contributes long term stability with poor initial color, as does the epoxy component. Cadmium furnished extremely good initial color and intermediate stability, while zinc provided very good initial color stability and very poor long term stability. The “zinc sensitivity” phenomenon described above applies to a lesser extent to cadmium as well.
The catastrophic degradation which occurs with zinc (sudden blackening & burning) is typical, and is due to the fact that zinc chloride, which is formed when the zinc salt’s carboxylic acid displaces labile chlorine on the polymer chain, is a strong Lewis Acid and a degradation catalyst for PVC. The phosphite component provides a measure of long term stability by itself.

In the figure, "Synergy: Component Combinations", the significant improvements in heat stability which can be obtained by combining the various stabilizer ingredients is seen. Ba/Cd and Ba/Cd/Zn systems benefit upon addition of the phosphite, which is believed to chelate or “tie up” zinc and cadmium chlorides formed during the process of stabilization. For this reason, phosphites are known to retard the “zinc burning” effects described above. The further addition of the epoxy component to a mixed metal system results in dramatic improvement in heat stability, more than simply additive and truly synergistic (recall epoxy performance alone).
It has been shown that a zinc sensitive resin can be made more “zinc tolerant” simply by washing the resin free of trace amounts of residual catalysts, suspending agents, or emulsifying agents. Vinyl acetate-vinyl chloride copolymers, as mentioned previously, are quite zinc sensitive (depending on acetate content) and use of zinc in the stabilizer system should be avoided. The one exception to this recommendation will be discussed under the subject of ‘Fillers’. Other types of copolymers generally respond to stabilizers in a manner similar to PVC suspension homopolymers, exhibiting varying degrees of zinc sensitivity. Most all of these copolymers (propylene, cetyl vinyl ether modified PVC) have greater inherent heat stability than the acetate copolymers. Bulk, or mass polymerized PVC exhibits heat stability quite similar to corresponding K-value suspension PVC resins, both responding well to a wide variety of mixed metal, organotin, and lead stabilizer systems. Emulsion polymerized PVC resins of today are mainly the “paste” or plastisol dispersion resins, having very small, smooth surfaced particles. Like suspension polymers, most dispersion resins respond well to mixed metal and organotin stabilizer systems. The older “high soap” emulsion resins, mainly European, did not respond as well to mixed metal stabilizers, relying more on organotin and organic amine types of stabilizers. Most of the emulsion resins of today have a much lower “soap”, or residual emulsifier content. This residual emulsifier probably explains why the use of minor amounts of emulsion resin in a general purpose suspension PVC calendering or extrusion formulation can help reduce plateout.

Modifying Resins— Several different classes of thermoplastic resins are used with PVC to enhance strength and/or processing and fusion of rigid PVC, as well as to modify properties of flexible PVC such as the retention of embossing during post-forming operations. These modifying resins include chlorinated polyethylenes (CPE’s), ethylene vinyl acetate/carbon monoxide terpolymers (Modified EVA’s), acrylonitrile-butadiene-styrene (ABS), methacrylate-butadiene-styrene (MBS), and acrylic polymers. Some of the newer thermoplastic elastomers that are PVC compatible (Alcryn) find occasional use in specialty flexible formulations. When incorporated with PVC, some of these modifiers can detract from heat and light stability to varying degrees. Generally, no basic change in the stabilizer system is required, although a slightly higher level of stabilization may be needed, depending on severity of the process. The EVA terpolymers and chlorinated polyethylenes are perhaps the least detrimental towards heat and light stability, and perform very well in rigid applications requiring good outdoor weathering. Acrylic polymer modifiers also are recommended highly for outdoor exposure applications. Some acrylic and ABS modifiers are good for clear vinyl applications (minimal stress-whitening), but detract somewhat from heat stability. The nitrile portion of ABS especially is thought to detract from PVC’s heat and light stability.

Impact modifiers can be classed as either “matrix” types (functioning via chain entanglement with PVC molecules), or “discreet particle” types (functioning via resin-rubber interfaces, or shock-absorbers to block crack propagation). EVA terpolymers and chlorinated polyethylene are examples of the former, and acrylic, MBS and ABS represent the latter types of modifiers.

The amount of impact strength obtained with these modifiers is as dependent upon processing conditions of extrusion or calendering as on the amount and type of modifier used. The degree of chain entanglement, or the presence of sufficient resin-rubber interfaces to act as “shock absorbers” during the process of absorbing and dissipating energy of impact requires optimum dispersion of the impact modifier. Too much or too little work applied during processing an impact modified PVC compound can furnish less
than optimum impact strength. Thus, a stabilizer/lubricant system which is quite lubricating may contribute to a condition of minimal work input, while a stabilizer/ lubricant system which has poor lubricity may contribute to a condition of overwork and high frictional heat buildup. Processing impact modified rigid PVC requires a delicate balance of “internal- external” lubrication, some of which may be contributed by stabilizer. More will be said on this under the “Lubricants” topic.

The use of certain acrylic polymers as processing aids is widespread. In addition to contributing towards smooth melt flow and good surface finish, they tend to promote earlier, faster fusion of PVC at a given temperature, and can even lower the fusion (or gelation) temperature of the compound. In addition to acrylics, poly (alpha methyl styrene) has been used on occasion as a process aid, requiring a higher use level to achieve equivalent performance to acrylic types.

**Plasticisers** - In over simplified terms, the word ‘plasticiser’ can be used to describe any material which is incorporated into a vinyl formulation to impart elastomeric properties of flexibility, elongation, and elasticity to the compound. Mostly liquid and sometimes solid in form, these materials are generally organic compounds of fairly low volatility. The most commonly used plasticisers include esters of aromatic and aliphatic dibasic acids, glycol diesters of monobasic acids, linear polyesters, epoxidized glycerides and mono-esters, phosphate esters, aromatic hydrocarbons and aliphatic chlorinated hydrocarbons.

Plasticisers are classified in terms of their efficiency, permanence, low temperature flexibility, compatibility, and solvating power on PVC resin. Generally, the greater the polarity, aromaticity or degree of chain branching, the greater will be the solvating power, compatibility, and efficiency of a plasticiser. On the other hand, low temperature flexibility performance is generally enhanced with a decrease in overall compatibility and solvating power within a series of plasticisers. The older, arbitrary definition of “primary” or “secondary” plasticisers is not entirely the case, since there exists a complete spectrum of compatibility covering the entire range of plasticiser types. There is not always a sharp, distinct difference between a “primary” and a “secondary” plasticiser, although the phthalates, trimellitates, adipates, and azelates would be considered in the primary arena, and hydrocarbons and chlorinated paraffins in the secondary arena by most.

With two notable exceptions, choice of stabilizer is not materially affected by the type or amount of plasticiser present in a formulation. Phosphates and chlorinated paraffins generally require the use of higher levels of epoxy co-stabilizer, and additional phosphite chelator in a mixed metal barium/zinc or calcium/zinc system. Oddly enough, both of these plasticiser types which are detrimental to heat stability also are among the few materials used to impart fire-retardancy to flexible PVC compounds.

Epoxy plasticisers (epoxidized soybean, linseed oils and tallate esters) are unique in the fact that they are almost universally used in flexible vinyl compounds at low (3-10 parts) as an auxiliary co-stabilizer with mixed metal stabilizer systems. Functioning as HCl acceptors primarily, epoxy plasticisers significantly enhance the heat and light stability of most mixed metal/phosphite stabilized compounds.

**Fillers** - Inert, solid inorganic mineral compounds, many occurring as natural products, are used in vinyl formulations as extenders for purposes such as reducing overall costs (except that pound-volume costing must be considered if appropriate to the product’s pricing), providing opacity, and achieving certain
desirable end-use properties. Such end-use properties might include abrasion resistance, tear strength, dry "hand", or feel to the touch, hardness and stiffness, and even- with alumina trihydrate(ATH)- fire retardency. Included in this group of materials, in addition to aluminum trihydrate, are a variety of grades of calcium carbonates and silicates such as clay, kaolin, talc, and (years ago, no longer used) asbestos.

The most commonly used filler in PVC formulations is calcium carbonate in its various forms (depending on source, ground limestone, marble, chalk, or precipitated). Although calcium carbonate itself does not detract from nor contribute to heat stability, there is a definite need to alter the metal ratio of mixed metal stabilizer systems with increasing levels of calcium carbonate usage to achieve optimum results. This effect is seen in the figure, “Effect of Filler on Zinc Sensitivity”. 

The low zinc- containing stabilizer exhibits better heat stability than the higher zinc stabilizer in a clear, unfilled PVC formulation, a somewhat zinc sensitive formulation. However, when that same formulation also contains a significant amount of calcium carbonate filler, the higher zinc-containing stabilizer furnishes better heat stability- both initial color and long term- than the low zinc stabilizer. Thus, we can see that with increasing levels of calcium carbonate filler, the need for zinc in the stabilizer system also increases. A further case in point to illustrate this is the recommended use of high zinc stabilizers with normally very zinc
sensitive PVC/acetate copolymers in highly filled flooring products (homogeneous vinyl floor tiles).

Flexible PVC products can use the lower cost 3-6 micron average particle sized calcium carbonate fillers, but rigid PVC benefits from use of finer 1-2 micron-or less- carbonate fillers, primarily to maintain impact strength. A 2 micron ground filler can have a small “top size” portion of 10-15 microns, and these “rocks” will kill impact.

The class of silicate fillers offers no great stability problem, and usually an increase in the amount of epoxy plus inclusion of an additional 0.5 part of a phosphite will be sufficient to overcome any stability problem that might occur.

ATH (alumina trihydrate) behaves very much like calcium carbonate in terms of stabilizer considerations. As a fire retardant/ smoke suppressant filler, ATH can be used in flexible PVC which is processed below the temperature at which ATH gives off its water of hydration ((425 deg.F.) . However, the rigid PVC processing “window” usually is close enough to ATH water emission temperatures to cause premature water release and porosity in the PVC product.

Pigments- Much has been published about the comparative heat stability, light stability, chemical resistance, oxidative resistance, etc. of the many organic and inorganic dyes and pigments commonly used in the vinyl industry. If the PVC stabilizer system has been selected for its maximum properties in terms of resin, plasticiser, filler content, process and end use properties, it will generally suffice in protecting the pigment as well. However, a couple of special cases need to be mentioned.

Metallic pigments to achieve unusual decorative effects, which are based upon finely divided aluminum, copper, gold, or bronze (especially the latter three), generally retain best color stability in the presence of alkaline stabilizers such as those based on barium alkyl phenate and specifically those alkaline stabilizers which contain little or no zinc. Lower epoxy use levels, and the use of inert lubricants such as mineral oil or low molecular weight polyethylene are also recommended in place of acidic lubricants such as stearic acid.

Fluorescent pigments are best stabilized for both heat and light exposure with alkyltin mercaptoester stabilizers. Good results are also obtained with high zinc mixed metal/phosphite systems.

Lubricants- One of the least understood for years, and yet most important aspects of PVC technology is the phenomenon of lubricity. The critical need to understand the nature of lubricity is especially important in rigid PVC technology, since it is difficult to separate completely lubricity and stability considerations during a rigid PVC process.
Lubricants can be classified to some extent by relating chemistry and behavior—the terms “internal” and “external” have been used to describe the nature of lubricants with respect to their use in PVC compounds. However, more realistically, there is a spectrum of lubricating behavior from the “internal” lubricity of polar molecules such as stearic acid, metal stearates, fatty acid esters, and glycerides to the materials containing both polar groups and long carbon chains giving balanced internal-external characteristics, and finally to the “external” lubricity of long chain hydrocarbon derivatives of paraffin oils, paraffin waxes and low molecular weight polyethylenes (oxidized and nonoxidized PE’s).

Internal lubricant behavior (showing some PVC solubility) contributes to lower melt viscosities and reduces internal friction between polymer molecules (a plasticising effect). Faster fusion is also seen with internal lubricity behavior.

External lubricants function essentially by their insolubility in PVC, migrating to the surface where they can reduce frictional drag between PVC melt and hot metal surfaces of the extruder, calender, etc. This type of lubricant behavior is very dependant on its molecular weight and melting point which determines where in the process (i.e. barrel, adapter, die) it will deliver the desired lubricity.

Current lubrication technology makes use of these internal and external characteristics in the form of specially designed lubricant “one-packs”, designed for specific processing and product applications.

Stabilizer selection in light of lubricity requirements is especially critical in rigid PVC processing. One example: Higher stabilizer levels are needed when N,N' ethylene bis-stearamide wax is used, due to the degrading effects of amides on PVC resin. Most all other lubricant types, internal or external, have no
adverse effects upon PVC heat stability, and respond well to normal stabilizer use levels. It is known that tin mercaptoester stabilizers contribute to lower melt viscosities than tin carboxylates, barium/zinc, calcium/zinc, and lead stabilizers. Most tin mercaptide stabilizers are essentially non-lubricating, but based on their compatibility and viscosity effects they might be thought to contribute some internal lubricity behavior. Therefore, tin mercaptides generally need more external lubricant in rigid PVC processing than the mixed metal or lead types.

Lubrication requirements for plasticized, flexible PVC are not nearly so critical. Stearic acid and stearyl alcohol are by far the most common lubricants in the industry, and work well with a wide variety of stabilizers including most mixed metal (Ca/Zn, Ba/Zn) systems. Stearic acid is especially recommended with alkaline stabilizers based upon barium phenates. Use of stearic acid should be avoided, however, with tin mercaptide stabilizers, since highly incompatible alkyl tin stearates may be formed which can result in exudation or “spew” in plasticised formulations.

Miscellaneous Formulation Components- Other additives used in many vinyl formulations include blowing (foaming) agents (to be covered under the subject of vinyl foams), wetting agents for plastisol viscosity control, biocides, anti-static agents, anti-fog agents for food wrap film, and U.V. absorbers (to be covered under the subject of light stability and outdoor weathering).

Care must be taken in selecting a stabilizer for vinyl compounds containing any of these miscellaneous components, since many of these additives may react with certain stabilizers to detract from heat stability or furnish colored reaction products.

For example, some anti-static agents - quarternary ammonium compounds- can reduce heat stability significantly. Some wetting agents also detract slightly from heat stability, requiring a slightly increased stabilizer level. Certain U.V. absorbers may form a yellow reaction product with alkaline stabilizers, requiring a higher stearic acid level to counteract this problem. Some U.V. absorbers (triazoles) may exhibit a “pinking” tendency with tin mercaptide stabilizers. The best approach in most cases is to evaluate heat stability and color retention of the formulation with and without the miscellaneous additive to pre-determine the extent of any potential problem.

PROCESS/ PRODUCTION VARIABLES:

Calendering- Most general purpose plasticised calendered film and sheeting, both unsupported and supported, is extremely well stabilized with liquid mixed metal barium-zinc or (where permitted) barium-cadmium-zinc/phosphite/epoxy systems, the selection of which depends upon such factors as resin zinc sensitivity, filler content, clarity needs, plate-out tendencies, etc. The newer barium-zinc, calcium-zinc, and zinc (cadmium-free) packages fortified with beta diketones, nitrogen heterocycles, or the new organosulfur/Zinc compounds also work very well in calendering of flexibles.

Special situations in flexible calendering would include production of high speed thin gauged calendered
film, which may require use of small amounts of powdered barium or zinc stearate boosters to the liquid system. These will add a touch of lubricity to handle the higher frictional heat buildup that occurs in the calender roll nips at thinner (below 10 mils) gauges.

------as far as I've gone so far------

A processing problem----Plate-out
End-use factors: Sulfur Staining and Clarity