

# PVC Handbook

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# 10 Flexible PVC

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## 10.1 Origins

Polyvinyl chloride (PVC) homopolymer is a semi-crystalline polymer with a relatively high room temperature tensile modulus of 2400 to 4140 MPa ( $3.5\text{--}6.0 \cdot 10^5$  psi), depending on formulation) that can be lowered by plasticizing entities to produce semi-rigid and flexible items. Many of these have turned out to be commercially useful and cost competitive. Use of other additives, in addition to plasticizers, is essential to making successful flexible PVC products. These include stabilizers, pigments, fillers, lubricants, and many specialty additives such as fire retardants, anti-microbials, UV-screens, and antistats for particular applications.

To put the development of flexible PVC in perspective, some historical facts are of interest. Of the seminal discoveries leading to successful flexible PVC products, some were empirical and others the results of classical theory-driven research. Space allows only a few of these milestones to be described here.

In Germany prior to World War I, the development of electric lighting resulted in a large excess of calcium carbide as acetylene lamps were phased out. Fritz Klatte, working for Chemische Fabrik Griesheim-Elektron, found that acetylene can react with HCl to form vinyl chloride monomer (VCM), which in turn, can be polymerized to PVC using free-radical initiators. Klatte was then commissioned to find uses for the hard, horny intractable PVC resin. He obtained several patents [1, 2], but Griesheim-Elektron let them expire in 1926. Klatte had shown promising leads but his team had not identified good enough plasticizers, heat stabilizers and process aids to make superior PVC replacements for celluloid, lacquers, oil cloth, coatings generally, fibers, and so forth.

Other German companies then took up the challenge and had developed commercial PVC formulations by 1939. Shortages of conventional materials during World War II led to practical uses for both flexible and rigid PVC in wartime Germany. Post-war allied studies of German industry publicized these world-wide, e.g., [3].

Between 1926 and 1933, Waldo Semon at BFGoodrich in the United States discovered that tricresyl phosphate (TCP) and dibutyl phthalate (DBP) were effective plasticizers for PVC. In addition, he determined that basic silicate of white lead was an adequate stabilizer to make processable flexible PVC formulations plasticized with TCP or DBP. Goodrich then patented some of these formulations and commercialized coated fabrics and films made from them and trade-named them Koroseal<sup>®</sup> [4, 5].

Supplementing the antecedent German work, which sought volume uses for acetylene, Carbide and Carbon in the United States sought outlets for their large excess of ethylene dichloride

(EDC), which was a by-product of their ethylene chlorhydrin manufacture. In 1930, they found that they could produce pure VCM by treating EDC with caustic soda. They made PVC homo- and co-polymers from the VCM and supplied samples to Waldo Semon and others.

General Electric developed plasticized PVC insulation and jacketing for electric wires and cables. They trade-marked these Flamenol®, reflecting their resistance to ignition compared to the then-standard flexible insulations and sheathings made from natural rubber.

In 1933, a patent covering the PVC plasticizer di-2-ethyl hexyl phthalate (known as DEHP or more often DOP) was issued to Lucas Kyrides of Monsanto Chemical Company [6]. Monsanto sold the patent to Union Carbide, because at the time Monsanto was more interested in developing plasticized polyvinyl butyral interlayers for automobile windshields and windows than in plasticized PVC.

Ironically, it was Monsanto's air-oxidation process for making inexpensive phthalic anhydride, which later made low cost DOP a reality in the United States [7].

T. L. Gresham at BFGoodrich ran extensive tests and identified DOP as the best available plasticizer for PVC homopolymers used for making flexible PVC.

Just as in Germany, World War II stimulated the development of uses for flexible and semi-rigid PVC in the United States, Great Britain, and other allied countries. This was driven by shortages of rubber, leather, and other naturally derived raw materials.

After World War II, it became obvious that many of the substituted plasticized PVC products had performance properties and costs superior to those of the natural items they had replaced. Many became established as accepted items of commerce.

## 10.2 Types of PVC Resins Used in Flexible Applications

The largest volume PVC resin type used in flexible and semi-rigid applications is aqueous suspension PVC homopolymer, made to have sufficient porosity in the particles to absorb enough plasticizer to meet the desired flexibility and hardness specifications of the intended end-product. For most flexible uses, the resins range from medium to high molecular weight. By normally accepted conventions this means from approx. 30,000 to approx. 60,000 number average molecular weight. In terms of commonly used tests based on dilute solution viscosity, this means from approx. 0.57 to 1.10 inherent viscosity, or from approx. 51 to 71 Fikentscher K [8].

Using a mercury intrusion porosimeter to measure resin porosity, it is common to require about 0.30ml/g or more for resins used for moderately flexible items made with monomeric plasticizers; and about 0.40ml/g or more for highly flexible items made with monomeric plasticizers and for items flexibilized with polymeric plasticizers. In addition to pore volume, pore diameter may be measured for PVC resins used in flexible products. Larger pore diameters contribute to faster uptake of plasticizers.

Specialty soft plasticized PVC compounds requiring excellent compression-set properties call for the use of ultra-high molecular weight PVC resins with high porosity. These may exhibit molecular weights as high as 150,000 number average.

Flexible PVC products injection-molded or extruded at very high shear rates may be made with low molecular weight PVCs having less than 30,000 number average molecular weight. However, using PVC resins with such low molecular weights sacrifices physical properties, including compression set, elongation at failure, tensile strength, tear strength, and fatigue resistance. It is difficult to make ultra-low molecular weight PVC resins having high particle porosities. Very low molecular weight resins are not used for highly flexible items, because items made with them are too weak.

When formulating flexible PVC compounds for specific exacting uses, many compromises are often involved in selecting the best resin. For instance, other things being equal, the higher the molecular weight of the chosen resin, the higher the processing temperature needs to be during fabrication in order to achieve optimal fusion. Also, for a given processing temperature, use of higher molecular weight PVCs tends to give lower gloss on a finished product. If low gloss is required on an extruded product, which otherwise calls for use of a medium molecular weight PVC, it is necessary to specify a specialty “low gloss” resin offered by a few PVC manufacturers.

The particle shapes, size limits, size distribution, and internal porosities of the PVC grains formed during suspension or mass polymerization processes are functions of many factors dealt with in other chapters of this book (see, e.g., Chapters 3 and 11). For flexible applications, particle sphericity tends to provide good bulk flow behavior along with efficient particle packing and higher bulk density in dry blends. Irregular, knobby resin particles, broad particle size distributions, and high particle porosity tend to give low bulk density and poor bulk flow behavior.

For flexible applications, a relatively narrow PVC particle size distribution is desirable and is mandated by many users' specifications. In the United States, a typical specification for general purpose PVC aimed at flexible markets is  $\geq 99.8\%$  particles must pass through a U.S. 40 mesh sieve, whose nominal openings are 420 microns (16.5 mils) square; 10% maximum by weight retained on a U.S. 60 mesh sieve, whose openings are 250 microns (9.8 mils) square; and 2% maximum through a U.S. 200 mesh sieve whose openings are 74 microns (2.9 mils) square. The aim point for average particle size (APS) is normally between 100 and 80 mesh. That is between 149 and 177 microns (5.9 and 7.0 mils). For special purposes, suspension and mass PVC resins may have their APSs skewed to finer or coarser numbers.

The differences between mixing and processing methods for general-purpose flexible PVC and plastisol techniques for making flexible PVC products are described in Section 10.4 and in Chapter 9.

The distinctions between PVC resins made for use in plastisols and general purpose PVC resins are addressed here. Plastisol resins are sometimes called dispersion resins, or, mostly in Europe, paste resins. They are made by emulsion, microsuspension, or special proprietary processes. Typically, they contain spherical, solid particles ranging in size from 0.1 to 1.1 microns in diameter. In bulk resin, these resin particles provide large surface area due to their small diameters. They are readily wetted by plasticizers due to their surfactant content and absorb some plasticizer during mixing. Because the particles are solid PVC, they absorb plasticizers quite slowly at typical ambient temperatures. The plastisol resins made by emulsion polymerization may be dewatered by spray drying or a combination of coagulation and conventional drying. Weak agglomerates of the basic emulsion resin particles are formed during drying. These are normally broken up to a substantial degree in grinding procedures before use of the

resins. Most PVC plastisol resins are fluffy, have relatively low bulk densities compared to general purpose PVCs, and poor bulk flow properties. In most cases, they have to be given antistatic treatments to get them to flow satisfactorily in bulk handling systems. Consequently, plastisol resins are often bagged by the manufacturer before shipment to the customer. The systems used for bulk handling of plastisol resins are specially designed for this purpose and usually are dedicated to particular plastisol resins, and only used in large volume applications.

Microsuspension PVC resins used in plastisols differ from their emulsion-polymerized counterparts both in particle size distribution and emulsifier content. Their emulsifier content is lower than that of most emulsion resins and this contributes to higher clarity in clear formulations, low moisture sensitivity of the end products, and little or no contribution to fogging in automobile interiors.

Another class of PVC resins made for use in plastisols is called plastisol-extender resins. These are solid particle resins made by suspension polymerization with particles finer than general purpose resins, but coarser than microsuspension plastisol resins. The rationale for the use of such resins in plastisols is at least threefold. First, they are less expensive to make than true plastisol resins. Second, due to their coarser particle size on average, they contribute to more efficient particle packing in a plastisol when used in conjunction with a standard plastisol resin. This allows higher PVC content in a plastisol of given viscosity. Third, use of extender resin in a plastisol usually gives a rougher surface finish with lower gloss when this is desirable. This is important in sheet flooring constructions and plastisol-coated metal siding, for instance.

Typical screen analyses for plastisol extender resins are: > 99.6% through 140 mesh, 5% maximum on 200 mesh and > 65% through 325 mesh, using U.S. standard screens. Their APS is thus equal to or less than 44 microns (1.7 mils), which is the size of the 325 mesh screen openings.

Specialty PVC resins are made for producing flexible PVC items by rotational molding from powders and powder-coating of pre-heated parts. Some of them are specialty copolymers designed for blending with specialty homopolymers aimed to achieve particular performance results.

Graft copolymers constitute another type of resin used for making vinyl TPEs and unplasticized flexible vinyl articles or lightly plasticized low extractibles flexible PVC. An example is Vinnol VK 801 listed as having 50% EVA content, and offered by Vinnolit (which was formed by the merger of Hoechst and Wacker's PVC operations).

Solution vinyl resins are a specialty dealt with in dedicated texts [9].

### 10.3 Particulate Architecture of PVC Resins Used in Flexible Products

This section deals with general purpose PVC resins made for use in flexible products. The particle architectures of other PVC resins are covered in Chapters 3, 9, and 11 of this book.

In the early years of the PVC industry, a common problem in the manufacture of flexible PVC items by calendering and extrusion was the occurrence of gel particles, often referred to as

“fisheyes”. These are relatively solid PVC particles, which do not absorb plasticizer as readily as the other resin particles in the formulation and which do not fuse readily at the processing temperatures used. Large fisheyes are the most objectionable.

As the technology of polymerizing VCM has improved, the occurrence of fisheyes in flexible products has become a less frequent or severe problem. But it still exists, because the most frequent cause of fisheyes in PVC is inadequate cleaning of polymerization reactors between batches. PVC particles that go through two or more polymerization batches tend to have reduced porosity for absorption of plasticizers and to contain enough cross-linked, insoluble PVC to interfere with normal fusion. PVC manufacturers, who try to save money by reducing the frequency and diligence of reactor cleaning, produce resins with unacceptable content of gels.

A critically important part of PVC resin morphology is its semi-crystalline nature. This is responsible for the resistance of flexible PVC to heat distortion, creep, and compression set. When plasticized PVC started replacing rubbers in insulation and sheathing for electrical wire and cable, rubber technologists asserted that no thermoplastic composition flexible and soft enough to satisfy wire and cable flexibility requirements could meet the required specifications for resistance to thermal distortion, cut-through, compression distortion, compression-set, agglomeration of multiple insulations within a cable, abrasion resistance, and so forth. They believed that only cross-linked rubbers could be soft and flexible enough and still maintain their integrity under harsh conditions of use and testing. They asserted that no thermoplastic such as plasticized PVC would replace cross-linked rubbers. But based on its physical and flammability properties, plasticized PVC took over most of the indoor wiring insulation and jacketing market in developed countries. It was after this happened that many of the reasons why plasticized PVC fulfilled these requirements were elucidated. Numerous thermoplastic elastomers (TPEs) have since been developed, which are both thermoplastic and resistant to compression-set, creep, abrasion, and thermal distortion.

The seminal discoveries of the micro-morphology of rigid and flexible PVC are dealt with in detail in Chapters 3, 9, and 12 of this book. However, a terminology rationalizing the behavior of plasticized PVC is presented here. Rational terminology describing the morphology of PVC suspension- and mass-polymerized resin particles was proposed by Geil [10]. The lower end of Geil’s size hierarchy also applies to emulsion- and micro-suspension-polymerized PVC resins. Table 10.1 is adapted from Geil.

The crystalline microdomains in plasticized PVC, which are interspersed between amorphous regions, act like cross-links in rubbers in resisting creep, compression-set, and heat distortion, except that they are thermally reversible. Most of these crystallites melt at processing temperatures and re-form during cooling of fused plasticized PVC melts. The melting and recrystallization behavior, however, is complex because PVC contains several different kinds of crystallites, which melt and reform over a range of temperatures. Their melting and reformation is affected by the kind of plasticizer present. For instance, “fast fusing” plasticizers, of which butyl benzyl phthalate (BBP) is an example, depress the melting temperatures of the crystallites, thus promoting fusion at lower processing temperatures. “Low temperature” plasticizers, of which dioctyl adipate (DOA) is an example, primarily plasticize the amorphous regions of the PVC and have little effect on crystallite melting temperature, thus requiring higher processing temperatures than fast fusion or general purpose plasticizers.

**Table 10.1** Size Hierarchy of PVC Particulate Phenomena

Term	Size	Description
Grain	70–420 $\mu\text{m}$ diameter	Free-flowing powder produced in suspension or mass polymerizations
Agglomerates of primary particles	3–10 $\mu\text{m}$ diameter	Formed during polymerization by coalescing of primary particles
Primary particles	1 $\mu\text{m}$ diameter	Formed at single polymerization sites by precipitation of newly-formed polymer into discrete molecular aggregates
Domains	0.1 $\mu\text{m}$ diameter	Observed after certain types of mechanical working of the PVC
Microdomains	0.01 $\mu\text{m}$ spacing	Crystallites capable of holding portions of tie molecules, which maintain integrity of primary particles and span between primary particles in well fused PVC
Secondary crystallinity	0.01 $\mu\text{m}$ spacing	Crystallites re-formed during cooling of a fused PVC melt

Antiplasticization by plasticizers is a phenomenon that PVC formulators must take into account. This is the stiffening effect of low levels of some plasticizers, which takes place after fusing and cooling a formulation. It occurs most often with fast fusing plasticizers, to a moderate extent with general purpose plasticizers, and much less with low temperature plasticizers. It is observed at plasticizer concentrations of approx. 1 to 15 parts per hundred resin (phr). But this range varies with plasticizer efficiency. Antiplasticization is explained as being mainly caused by the promotion of crystallite formation by low levels of plasticizers without an offsetting plasticization of the amorphous regions, which occurs at higher plasticizer levels. It must be noted that these extra crystallites are of the low melting type and do not raise the heat distortion temperature of PVC, which is reduced by as little as 1 phr of most plasticizers or plasticizing stabilizers, such as the thiotins. Other factors discussed in the literature as contributing to antiplasticization effects are hydrogen bonding, Van der Waals forces, steric hindrance, small, localized increases in molecular order, and decreased free volume [11, 12].

Many authors have contributed to understanding the relationships between PVC particle morphology, fusion, and the processing rheology of PVC. Some of these are Collins and Krier [13], Berens and Folt [14], Singleton and Isner [15], Pezzin [16], Collins and Daniels [17], Lyngaae-Jorgensen [18], Summers [19, 20], and Rosenthal [21]. Their original findings relate to both rigid and flexible PVC.

## 10.4 Favored Processing Methods for Flexible PVC

The natures of the PVC resins and other additives used in flexible PVC compounds have conditioned the selection of efficient material handling procedures for making the primary mixes. The most common processing type is “dry blending”, also known as “powder mixing”. More than 85% of suspension and bulk PVC resins are initially processed by dry blending.

Historically, large volume, jacketed ribbon blenders and various other kinds of available mixing equipment were used. For flexible PVC formulations using liquid plasticizers, resins with sufficient porosity to absorb the liquids are intermixed with the other ingredients to get them mutually well dispersed down to the particulate level. The desired resulting product is a free-flowing powder. For most formulations, it is necessary to heat them during mixing to facilitate absorption of the plasticizers into the resin and to avoid loss of product through formation of undesirable lumps of wetted pigments and fillers. The main drawbacks to the large ribbon blenders were that cycle times were surprisingly long to achieve good blend uniformity and it required considerable technical effort of a largely empirical nature to determine the optimal order and timing for addition of individual ingredients. It was not unusual to produce a fair amount of off-grade product during the process of mixing cycle optimization when new formulations were introduced.

Much theoretical work has been done on dry blending of flexible PVC formulations. Diffusion of liquid plasticizers into PVC resin particles is a kinetic process whose rate varies inversely with the viscosity of the plasticizer [22]. During dry blending, liquid plasticizers penetrate the amorphous matrix surrounding the crystallites in the PVC resin particles. The crystallites remain intact because of the thermodynamic barrier which prevents fusion until a certain temperature is reached. This depends on the particular plasticizer or plasticizer mixture being used and the molecular weight of the PVC resin. While studying the Flory-Huggins interaction parameter,  $\chi$ , for various plasticizers with PVC, Anagnostopoulos et al. [23], developed a microscope hot-stage fusion test, whereby the temperatures at which PVC resins of different molecular weights fuse in particular plasticizers are readily measured. These fusion temperatures are higher than dry blending drop temperatures.

A dry blend is a non-fused mixture of PVC, plasticizer, and other ingredients. Park published a method for running the pressure stain test for PVC dry blends [24], which determines the point in a commercial dry blending cycle at which the blend no longer stains brown paper or cigarette paper sheets between which it is pressed. This correlates with the small-scale laboratory dry time test ASTM D2396.

From a practical viewpoint, a dry blend cycle is complete when the dry blend, after cooling, flows well through a funnel or an extruder hopper and does not cake during storage. The pressure stain test is a way of predicting when this state has been reached while the blend is still hot and in the blender. Commercial blenders are stopped during a cycle and a “thief” is used to take small samples for testing.

Dry blends of plasticized PVC formulations are over-dried if they are dusty and fuse with more difficulty in subsequent processing operations, such as extrusion, than a blend made with a shorter dry blending cycle, which is slightly damper and less dusty, but still has good bulk flow and non-caking behavior.



Low speed dry blending mixers are generally of the ribbon mixer type. These are bulky semi-cylindrical horizontal mixers supplied with a jacket surrounding the side and bottom surfaces through which heat or cooling can be applied. For mixing, radial blades are mounted on a horizontal rotating shaft, which may turn at 40 to 70 rpm.

Intermediate speed dry blenders generally consist of a horizontal cylindrical jacketed chamber with axially mounted blades, which can be run fast enough to achieve fluidization of the PVC during blending.

Where the investment can be justified, batch high speed, high intensity, dry blending mixers are used for flexible PVC. Typically, these consist of a vertical drum with a dish bottom through the center of which a drive shaft penetrates. One or more sets of mixing blades are attached to the drive shaft. A baffle penetrates the top of the mixer, which can be tightly sealed to the drum. By running the drive shaft at speeds appropriate for the particular formulations being mixed, mixing occurs with the generation of sufficient frictional heat to raise the batch temperature to a desired drop temperature, such as 105 °C in 4 to 8 minutes. These intensive mixers all have Froude numbers\* much greater than 1. Typical shaft speeds are 500 to 1200 rpm with blade tip speeds between 10 and 50 m/s (33 and 164 ft/s). Typical batch capacities are 80 to 200 kg (176 to 440 lb). Some of these mixers are designed to sustain high vacuum or air purge during mixing for removing traces of unwanted volatiles such as moisture or residual vinyl chloride monomer [25]. The PVC and other ingredients are fluidized during blending in these mixers.

The high speed mixers generally dump their batches into lower speed jacketed rotary coolers having Froude numbers less than 1. The coolers introduce little frictional heat and cool by conduction into their cold water jackets. To avoid adventitious condensation of moisture from the ambient air, freezing brines are not used in these cooler jackets. Specialty dedicated blending procedures are used for flexible PVC compounds made with solid plastifiers, polyolefin elastomers (POEs), and compatibilizers.

$$* \text{ Froude number} = R \omega^2 g$$

where

$R$  = blade radius

$\omega$  = angular velocity, radians/s

$g$  = gravitational acceleration in consistent units

Trade names for typical intensive mixers are Henschel, Papanmeier, Welex, and Littleford.

To shorten mixing cycles, high viscosity plasticizers (polymeric liquids) are normally preheated before addition to the mixer.

In many factories the cooled dry blend is air conveyed to interior storage before being fed to fabrication equipment or intermediate processing units. It must not "cake" during storage, and it must flow readily and uniformly in the feed hoppers of equipment such as extruders and proportioning devices, for example, those used for color control operations.

From interim storage, dry blends are conveyed to fluxing devices, such as compounding extruders, Banbury mixers, Farrel Continuous Mixers, Buss Ko-Kneaders, and fusion systems made by Coperion, Krauss-Maffei, Leistritz, Reifenhauser, and many others. The hot, fluxed

PVC may then go to pelletizing units and be sold as compound pellets. Alternatively, it may be fed directly to fabricating equipment such as extruders, calenders, or injection molding presses.

Another type of mixing for preparing flexible PVC goods involves compounding of liquid plastisols. This is done in liquids mixing equipment using plastisol grade PVC resins, suitable plasticizers, and other additives such as stabilizers, fillers, pigments, and other ingredients. These may include viscosity modifiers, air release agents and thinners, which are dedicated for use in plastisols, modified plastisols, and organosols, discussed later in Section 10.5 and Chapter 11.

Inverted conical Nauta mixers, pony mixers, high speed Cowles Dissolvers, medium speed Ross Power Mixers, and three-roll mills are typical of the mixers used for manufacture of plastisols.

In most cases, plastisols are de-aerated after mixing and stored at controlled temperatures, preferably at or below 23 °C (73 °F), to prevent heat-induced viscosity build-up and other changes in their desired rheology caused by aging.

Plastisols are fabricated into end-use items by liquids-forming procedures followed by gelling and fusion in ovens. Plastisol-derived sheet flooring is the largest volume use for plastisols. Many of these flooring constructions are sophisticated, involving a flexible backing covered with a foamable plastisol on which a design is printed with some inks containing a foaming inhibitor and overlaid by a clear plastisol wear layer.

## 10.5 Designing Flexible PVC Compounds

### 10.5.1 Formulation Development

There are two general approaches to formulating flexible vinyl materials. When a project involves a novel untried concept for which the technical requirements of the product are unknown, a set of tentative needs is “guesstimated”. Trial formulations, whose properties bracket the tentative needs, are developed and parts or items submitted to field trials. The process is iterated until a satisfactory product is developed or the project is abandoned as impractical or too costly.

When the technical and economic requirements for the new product are known and considered feasible using flexible PVC, these are listed and used as guidelines. They involve physical and optical properties, stability to heat and light, decorative, electrical and toxicological requirements, density, odor, allowable cost, and so forth. Specifications and necessary qualification tests must be defined, including needs to run field trials at customers or evaluations at outside testing services, such as Underwriters’ Laboratories or suppliers’ or customers’ laboratories. The total cost of the development program and the potential profitability of the new product need to be estimated to justify proceeding with development.

In developed countries, the existing markets for flexible PVC are defined and competitive. In some cases, several plastics and plastic alloys, whose economics are close together, are competing and flexible PVC is simply defending or increasing its market share.

In undeveloped countries, flexible PVC has many opportunities to improve the standard of living of the people by satisfying unfulfilled needs and replacing natural materials, over which flexible PVC has some clear-cut advantages.

When the technical requirements for a new product cannot be satisfied by flexible PVC, it is industry practice to refrain from submitting a defective vinyl part for trial. There should be at least a 50% probability of success to justify submittal of trial items.

### 10.5.2 General Problems in Formulation Development

In the flexible PVC industry, the term compounding has meanings specific to whether it is applied to solid or liquid systems. For solids, the steps generally are mixing a dry blend from solid and liquid ingredients, or mixing a wet blend, then fluxing the dry or wet blend until it will flow properly in forming equipment, shaping the melt into an end product, and cooling the hot product before it loses its desirable shape.

In the case of plastisols and organosols, compounding means mixing the solid resin and other solid ingredients uniformly into liquid plasticizers and other liquid ingredients so as to achieve a targeted rheology suitable for follow-up liquids-forming operations (reverse roll coating, spread-coating, rotational molding, dip coating, spray coating, strand coating, injection molding, etc.), followed by fusion in a suitable oven or microwave treatment, and finally succeeded by cooling before the product loses its desirable form and shape.

For PVC latexes, ingredients are normally added in waterborne solution, emulsion, or dispersion and mixed into the base latex under gentle agitation, so that it does not coagulate the latex or mixture of latexes. The compounded latex is then applied to the substrate to be treated by common latex application methods, such as dipping, impregnation, coagulation, reverse roll coating, spraying, and so forth. The water is then evaporated and, if necessary, the product is fused and cooled.

When more than one company is involved in developing a product, the importance of accurate and complete inter-company communications cannot be over-emphasized. An example of a product failure, which was corrected, was the manufacture of a large number of electric alarm clocks with high-impact polystyrene (HIPS) cases around which the vinyl-jacketed cords were tightly wound before packaging them. After some of the clocks were sold it was found that the HIPS cases had all been marred by migration of plasticizer from the cord jackets. The maker of the cords had not been told that their jackets were going to be in direct contact with HIPS. The problem was solved at a modest increase in cost of the cords by replacing the commodity phthalate originally used with a blend of higher molecular weight phthalate and trimellitate and modifying the packaging procedure.

The vinyl industry has sometimes been victimized by callous formulators, who make items from the cheapest formulation that satisfies initial requirements without providing suitable in-use and aging behavior. An example with vinyl-coated bookbinders was one in which the vinyl coating was plasticized with di-hexyl phthalate. When placed in contact with photocopy inks this binder "lifted" the inks and ruined the copy's appearance. A second example was a "non-migratory" binder plasticized with epoxidized soy bean oil (ESO) as sole plasticizer at about 50 phr. Initially, this binder exhibited exemplary non-migratory behavior. But after

about a year of exposure to fluorescent light and some sunlight, the binders with this composition were ruined by tacky exudates which gave them a surface like fly paper. The problems were solved at some increase in formulation cost by using a combination of medium molecular weight polymeric plasticizer and a high molecular weight phthalate for the non-migratory binder and just a high molecular weight phthalate for the regular binder.

Non-availability of optimal raw materials at competitive cost is a problem frequently faced by vinyl compounders. For instance, compounder A may have bulk storage for PVC resins J, K, and L along with plasticizers P, Q, and R. Compounder B has more extensive storage facilities and greater purchasing power for getting special deals on resins, plasticizers, and other raw materials. Compounder A, due to his lower overhead costs, has an advantage as long as he confines himself to his niche markets. But compounder B's products have better cost/performance in other markets due to his superior raw materials situation and more versatile compounding equipment.

In competitive situations, compounders may need to modify their mixing and fluxing procedures or upgrade their equipment. For instance, slow dry blending may be causing a production bottleneck caused by the use of a polymeric plasticizer or a slow dry blending monomeric plasticizer, such as DTDP. One approach is to reformulate, but the bottleneck may be more readily eliminated by pre-heating the plasticizers before adding them to the mixer and/or use of a faster blending, more porous PVC resin.

It is a luxury to work in a plant where the mixing, fluxing, and forming equipment are all optimized for the products being manufactured. In older plants, it is common practice to optimize throughput by selecting raw materials. For these situations, compounders use the lowest molecular weight PVC resin that satisfies end-use requirements, along with as much process aid that economics allow, and as fast-fusing a plasticizer system that is consistent with end product requirements.

In calendering plants producing thin gauge films, it is normal to pass the fluxed feed through an extruder-strainer to eliminate adventitious metal contamination, which could cause very expensive damage to the finishing rolls of the calender. These strainers need to be designed for the rheology and throughput of the stocks run on the calender. A strainer designed for highly flexible formulations tends to overheat rigid stocks at typical desired throughputs. This may limit the flexibility of calender lines with regard to switching back and forth from flexible to rigid stocks. Similarly, continuous compounding mixers need to be designed for the rheology and the throughput of the stocks they are handling. Equipment designated to the manufacture of diced or pelletized compounds also needs to be suited to the rheology of the range of compounds being manufactured in order to achieve optimal through-puts. Versatility can be achieved by stocking a range of parts for compounders, pelletizers, and dicers.

End-product performance failures in terms of resistance to compression-set, retention of elongation after oven aging, fatigue after repeated flexing, abrasion resistance, plasticizer extraction by oils or fats, and environmental stress-cracking of rigid plastics in contact with a flexible PVC part often can be corrected by switching to higher molecular weight PVC resins in the rigid PVC, higher molecular weight plasticizers, and/or introducing specialty additives such as process aids or "plastifiers" in place of part of the plasticizer system in the flexible PVC. To maintain throughput in spite of higher melt viscosity, the formulator usually has to adjust the stabilizer and lubricant systems to accommodate higher stock temperatures.

For composite products, such as coated fabrics or carpets backed with flexible vinyl materials, either by plastisol coating or laminating, the fusion temperature of the vinyl must not exceed the tolerance of the fiber in the fabric or carpet. This is critical with some polyolefin fibers. Suitable low fusion temperatures can often be achieved in the vinyl composition by using copolymer resins and fast-fusing plasticizers such as BBP or DHP.

For vinyl automobile undercoats and sealants, paint oven temperatures dictate selection of low-fusing resins and plasticizers. Fully fused vinyl undercoats survive considerable abuse and prolong the life of a vehicle, particularly in regions where roads are heavily salted in winter. Poorly fused undercoats fail prematurely.

In flexible PVC products which are foamed during processing, whether they use hot melt or plastisol technology, the fusion characteristics of the resin-plasticizer system must be matched to the behavior of the blowing agent-kicker-stabilizer in order to achieve manufacture of good quality uniform cell-size closed-cell foams. For consistently satisfactory results, excellent control of the rheology and time-temperature profiles is essential.

Extrusion, calendering, injection molding, thermoforming, and compounding processes are sometimes marred or shut down by a phenomenon known as plate-out. This comprises the formation of sticky deposits on the hot surfaces of processing machinery, including mill rolls, calender rolls, extruder screws, dies, molds, and so forth. The surface appearance of finished goods deteriorates in the early stages of a plate-out problem. If this is not recognized and corrected, it may lead to catastrophe such as “shipwreck” on a fast-running calender. This occurs when the calender web stops releasing from the final calender roll and folds back into the calender nip. This often causes severe degradation before the calender can be shut down. An expensive and labor-intensive clean-up always follows a calender “shipwreck”.

Plate-out is caused by precipitation and transfer of oxidation and/or hydrolysis products from components of the formulation (usually the stabilizer and lubricant system). The initial plate-out, if not observed and eliminated, then proceeds to build up by occluding solids from the formulation such as colorants, fillers, and smoke- and flame-retardants. If ignored, the plate-out eventually stops the plastic product from releasing from the hot/coated metal or releases a badly marred product from a coated mold, calender roll, or die. Products marred by plate-out usually exhibit poor printability.

Sometimes, plate-out can be eliminated “on the run” by temporarily increasing the amount of an abrasive, such as talc, or lubricant such as stearic acid, in the formulation. Plate-out is prevented in some formulations by including a small amount of a scouring agent such as talc or some grades of silica. Often, an operation plagued by plate-out has to be shut down and the affected metal surface manually or operationally cleaned. Raw materials suppliers should be consulted about persistent plate-out problems. Lippoldt [26] published an extensive study of plate-out.

Pollution regulations differ so widely from country to country and region to region that general rules for coping with them are meaningless. Processors need to dispose of solid, liquid, and gaseous wastes and vapors generated in the processing of flexible PVC in compliance with local regulations (see Chapter 18).

### 10.5.3 Properties Often Specified for Semi-Rigid and Flexible PVC Products

Tensile strength and elongation at failure (ASTM D638) depend primarily on the level and type of plasticizer or other flexibilizer in the formulation, but also on resin molecular weight. Higher molecular weight resins in fully fused formulations give higher tensile strength and elongation at failure. 100% Modulus, defined as tensile stress at 100% elongation, is a useful measure of the stiffness of plasticized PVC, because it is relatively easy to measure accurately and reproducibly. For historical reasons, DOP is generally recognized as the benchmark plasticizer for PVC. With a medium-high molecular weight PVC, at 23 °C, DOP at 25 phr gives a 100% modulus of about 22.8 MPa (3300 psi), which is classified as semi-rigid. Between 35 phr DOP and approx. 85 phr DOP (100% modulus 4.48 MPa or 650 psi), PVC is considered flexible. Above 85 phr DOP, PVC is called highly flexible.

When comparing the efficiencies of different plasticizers, substitution factors (SFs) compared to DOP are generally used. However, most authors calculate these from Shore hardness measurements, which do not correlate exactly with 100% modulus, see Chapter 5 for more details.

The brittleness temperature of flexible PVC is generally measured by ASTM D-746, which is a cold impact test run on specimens punched from standard test sheets  $1.9 \pm 0.25$  mm ( $75 \pm 10$  mils) thick. However, on calendered PVC films, some people prefer to use the Masland Impact Test (ASTM D1790). This test is run on films 10 mils (0.25 mm) or less in thickness under specified impact conditions. In this test, the results are sensitive to the direction of sampling and the direction of fold due to the molecular orientation effects of calendering. Outside the United States, local testing procedures may be preferred.

In commercial laboratories the low temperature properties of flexible PVC are often estimated from stiffness measurements run by ASTM D 1043, which measures apparent modulus of rigidity,  $G$ , at different temperatures. The way D1043 is run, the angular deflection may extend beyond the elastic limits of the plastic at lower temperatures, so that the result is “apparent” rather than an actual modulus of elasticity,  $E$ , as measured by ASTM D 747. To convert  $G$  to  $E$ , the simplifying assumption is made that  $E = 3G$ , which is only true if Poisson’s Ratio for the material under test conditions is 0.5. The temperature at which  $E = 931$  MPa (135,000 psi) is reported as  $T_p$ , the flex temperature, which is the temperature at which the material is considered to have lost most of its elastomeric properties. Sometimes  $T_u$  ( $E = 6.90$  MPa or 10,000 psi), regarded as the upper end of a material’s useful temperature range, is also reported.

Academic laboratories generally use more precise methods of measuring moduli as functions of temperatures.

Abrasion resistance of flexible PVC is often measured by the Taber Abrasion Test (ASTM D 4060). Results are reported as weight loss per 1000 cycles under conditions agreed to between the interested parties. Results are important for automobile undercoatings, boot and shoe soles, floor coverings, mine belts, and electrical cords for use under harsh conditions.

The hardness of flexible PVC materials is commonly measured by Shore Hardness (ASTM D 2240) using the A scale. Sometimes the D scale is used on semi-rigid compounds with plasticizer levels at or below 40 phr DOP equivalent. Conditioning of test specimens at the test temperature is critical. Aging after processing is also very important. This is explained as being due to the slowness with which PVC crystallites reform after processing. For accurate

results, at least one week of aging at 23 °C (73 °F) is recommended. Hardness readings increase with age after molding or other processing. Note also that Shore hardness readings drop rapidly during the first several seconds after specimen contact. For vinyl plastics, ASTM specifies taking Shore A hardness readings after 15 seconds. However, many commercial laboratories use 10 second Shore hardness. Test sample thickness is critical. ASTM specifies using specimens molded to 0.64 cm (0.25 in) thickness. On calendered or extruded films and sheets, many laboratories stack several thicknesses, but this is less precise than using specimens molded to 0.64 cm thickness.

In commercial quality control testing, operators never wait until Shore hardness has stabilized before testing. They specify definite aging and conditioning periods of usually less than a day. In the United Kingdom, British Standard Softness (B.S. 2782:32A) is generally specified. This test correlates well with 15 s Shore A hardness in the sense that a plot of Shore A hardness against British Standard softness is a straight line. The same considerations regarding aging and conditioning of flexible PVC specimens apply as for Shore Hardness testing.

For flexible PVC compounds used as primary insulation on electrical wires and for electrical tapes, electrical properties are critical. Tests commonly used include dielectric constant (ASTM D150), dielectric strength (ASTM D149), and volume and surface resistivity (ASTM D 257). The Underwriters' Laboratories Insulation Resistance Test is specified for insulation compounds to be used on wires slated for use in wet locations.

The fire resistance of most flexible PVCs is less than that of rigid PVC. However, formulations can be devised to meet stringent flammability requirements, such as those for plenum cables. These require enough flexibility for installation in confined spaces and must also pass the UL-910 (NFPA 262) test [27]. Other flammability tests often used on flexible PVC products include: the UL-VW-1 Vertical Wire Flame Test; the Oxygen Index Test (ASTM D2863); the DOT 302 MVSS Test for materials used in automobile interiors; the UL-94 Test run in the horizontal or vertical modes; the UL Vertical Tray Flame Test (UL 1581 for tray cables); and the UL-1666 Test for riser cables.

The Cone Calorimeter Test, ASTM E1354, can be used to rank small samples of flexible vinyl materials for rate of heat release after ignition, ease of ignition, and emission of obscurational smoke. The test is versatile, because the heat flux to which samples are exposed can be varied from about 10 to 100 kW/m<sup>2</sup>. Rate of heat release, sample mass loss rate, and smoke are measured or calculated from measured parameters.

For smoke evolution, the NBS Smoke Chamber Test (ASTM E662) is still used, because many laboratories have the equipment. Cone calorimeter results are acknowledged to be more meaningful.

Measuring the toxicity of smoke from burning PVC is complex and has been controversial. It is discussed in Chapter 13, along with general flammability testing issues.

Other tests used on flexible PVC products include retention of elongation after oven aging, resistance to extraction of plasticizers by chemicals, weatherability, stain resistance, and effects on taste and odor of foods packaged in flexible PVC. For niche products, many other specialized tests are used. Physical and electrical testing of PVC are discussed in Chapter 12.

## 10.6 Additives Used in Flexible PVC Compounds

### 10.6.1 Liquid Plasticizers and Solid Flexibilizers

Primary plasticizers are the principal additives responsible for flexibilizing PVC. These are classified as monomeric, polymeric, epoxy, and specialty flame-retardant plasticizers. They are low volatility liquids whose polarity and other characteristics are such that they are sufficiently compatible with PVC not to be readily squeezed out of plasticized PVC by moderate pressure [28].

Secondary plasticizers are low volatility liquids whose compatibility with PVC is such that they can be used along with primary plasticizers as part of the plasticizer system, but which exude if used as sole plasticizer. Chlorinated paraffins are common examples of secondary plasticizers for PVC, used because they are low in cost and less flammable than most primary plasticizers.

There are several types of solid flexibilizers for PVC, which include compatible nitrile rubbers, compatible polyurethanes, compatible polyesters, ethylene-carbon monoxide-vinyl acetate terpolymers, and some poly-acrylates. Many people refer to these materials as PVC “plastifiers” to distinguish them from liquid plasticizers. These solid materials are chiefly used in PVC thermoplastic elastomer (TPE) compounds and specialty PVC materials, some with low flammability and low smoke evolution, for use in applications such as plenum cables. The volume cost of these plastifiers is higher than that of most plasticizers. When used as sole flexibilizer for PVC, plastifiers give compounds with higher melt viscosity than corresponding plasticized compounds of equivalent hardness and flexibility. Plasticizers for PVC and theories of plasticization are discussed in detail in Chapter 5.

A few additional practical comments will be offered in the following. The definition of plasticizers adopted by IUPAC in 1951 is still generally accepted: a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second order transition, or lower the elastic modulus of a product. In comparison, a process aid improves processability without necessarily reducing melt viscosity or the stiffness of the product.

Practical requirements for a successful plasticizer for PVC are that it be cost-effective, stable, low in color, compatible with PVC, readily dispersible in PVC, low in volatility, low in odor, low in toxicity, have good permanence, and must not interact unfavorably with other needed formulating ingredients or otherwise compromise the end-use properties of the product in which it is employed.

Plasticization theory works reasonably well in quantifying the behavior of single plasticizers in PVC. When mixtures of plasticizers of different chemical families are used, the correlations between pragmatic performance parameters and scientific measurements on idealized systems become too loose to maintain the latter as standards for predicting the performance of plasticized PVC in the marketplace. However, on individual new plasticizer candidates, calculated or measured entities such as hydrogen bonding parameters, Flory-Huggins interaction parameters, dielectric constants, dipole moments, and solubility parameters can be used to predict compatibility with PVC.



Primary plasticizers used in PVC fall into the following chemical families: dialkyl ortho-phthalates, alkyl benzyl phthalates, dialkyl tere-phthalates, epoxides, aliphatic carboxylic diesters, polyester-type polymeric, phosphate esters, trimellitate esters, benzoate and dibenzoate esters, alkyl sulphonic esters of phenol and cresol, and miscellaneous types.

The 2003 Modern Plastics World Encyclopedia lists 402 plasticizers of which 279 are indicated to be compatible with PVC. Forty suppliers are listed.

Dialkyl ortho-phthalate esters are the most frequently used plasticizers in PVC applications. The alcohols range from hexyl ( $C_6$ ) to tridecyl ( $C_{13}$ ), and may be linear or branched. Increasing the degree of branching in the alcohol gives a plasticizer with higher volatility, greater susceptibility to oxidation, poorer low temperature brittleness in PVC, and higher volume resistivity in formulated PVC. Di-2-ethyl hexyl phthalate, also known as DEHP or DOP, is the industry standard general purpose (GP) plasticizer against which other dialkyl phthalates and PVC plasticizers generally are compared via efficiency factors (EF).

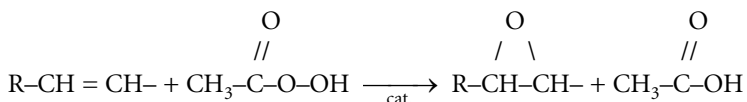
In addition to making recommendations on how to use plasticizers based on their experience, several plasticizer suppliers calculate the exact concentrations of their plasticizers required with a standard PVC resin to produce a desired set of physical properties, if it is attained in PVC plasticized with their products. The selection of the best phthalate plasticizer to use for a particular application is guided by economics, toxicological regulation (if required), ease of processing, and performance in end-use.

Aliphatic carboxylic diesters, such as the phthalates, are generally identified by acronyms. They are based on aliphatic dibasic acids esterified by alcohols ranging from  $C_7$  to  $C_{10}$ . The dibasic acids have carbon numbers varying from  $C_5$  (glutaric) to  $C_{10}$  (sebacic). Di-2-ethylhexyl adipate is known as DOA. The azelates and the adipates do not lower the melting points of PVC crystallites as much as the corresponding phthalates do, but they flexibilize the amorphous regions of the PVC more efficiently, and they are lower in molecular weight and specific gravity. Hence, they impart higher flexibility weight-for-weight and better low temperature properties. DOA is less compatible with PVC than DOP and is considerably more volatile. DOA is regulated by FDA for use in produce-wrap and meat-wrap films.

Most polyester-type polymeric plasticizers are condensation products of glycols with dibasic organic acids. 1,3 butylene glycol and adipic acid are the most often used starting materials.  $C_8$  or  $C_{10}$  alcohols are commonly used for terminating the polymerizations at average molecular weights between 1,000 and 8,000. Acid-terminated polymeric plasticizers are less environmentally stable than their alcohol-terminated analogs. The chief advantage of polymeric plasticizers over general purpose monomeric plasticizers is greater permanence. The chief disadvantages are higher cost, lower plasticizing efficiency, poorer low temperature properties, and reduced environmental stability of end products exposed to combinations of warmth, humidity, UV light, and/or active microbial cultures. Practical formulations often contain mixtures of polymeric and monomeric plasticizers.

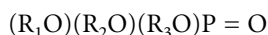
Trimellitate ester plasticizers are made by reacting trimellitic anhydride with plasticizer-grade alcohols. Tri-2-ethyl hexyl trimellitate is known as TOTM. These esters represent the state-of-the-art in low volatility monomeric plasticizers. Their principal uses are in 90 °C- and 105 °C-rated electrical wire insulations and jackets and other applications requiring plasticizers volatility lower than is attainable with higher molecular weight phthalates. Adams reviewed the status of trimellitate plasticizer use in the United States [29].

Epoxy plasticizers have oxirane oxygen groups in their molecules formed by the epoxidation of olefinic double bonds in their starting raw materials:



They are used as co-stabilizers along with suitable mixed metal stabilizers and some of the newer types of stabilizers. Epoxidized soy bean oil (ESO) and epoxidized linseed oil (ELO) are the most widely used epoxides. They have the disadvantage of being food nutrients for molds, some bacteria, and fungi. Sound formulators use epoxides at low levels because the oxirane oxygen group has a strong compatibilizing action with PVC. Use of higher levels of ESO or ELO risks formation of tacky “spew” resulting when the oxirane oxygen is photo-oxidized or hydrolyzed. To get the stabilizing action of oxirane oxygen without the risk of exudation or microbial attack, some formulators use epoxy resins even though these cost more than ESO or ELO.

Phosphate ester plasticizers made from phosphorus oxychlorides have the general structure:



Where,  $\text{R}_1$ ,  $\text{R}_2$ , and  $\text{R}_3$  are alkyl or aryl moieties. Numerous triaryl and alkylaryl phosphate plasticizers are available. They are more expensive than phthalate esters, have excellent compatibility with PVC, and burn with lower heat release than phthalates. The principal use of phosphate esters is in flame-retarded and smoke-suppressed formulations.

Dipropylene glycol dibenzoate exemplifies the benzoate ester plasticizers, which are used mostly in stain-resistant flooring.

Several miscellaneous plasticizers are used enough to be worth mentioning. Some citrate esters, such as acetyl tri-*n*-hexyl citrate and butyryl tri-*n*-hexyl citrate, find specialty uses in some blood bags and food wraps. Citrates are also used in toys produced by the plastisol process, where the toy is intended for use by young children. Polymerizable plasticizers are available for specialty applications such as insulation on electrical wires, which have to be connected by soldering and where retraction of the insulation due to heat must not occur. Alkyl sulfonate esters of phenol are sold in Europe under the trade name Mesamoll®. Texanol Isobutyrate® (TXIB) is used as a volatile, viscosity-reducing plasticizer/diluent in plastisols for flooring sheet-goods and coil coatings. Specialty flame-retardant plasticizers are exemplified by Great Lakes DP-45, which is a tetrabromophthalate ester with outstanding fire-retardance and low plasticizing efficiency due to its high molecular weight and high specific gravity. Secondary plasticizers, extenders and diluents include chlorinated paraffins, naphthenic hydrocarbons, alkylated aromatics, and some linear paraffins.

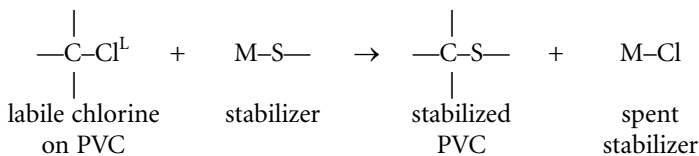
### 10.6.2 Lead-Based Stabilizers

Stabilizers have been used in flexible PVC compositions to prevent degradation during processing and forming into finished shapes. Mainly due to pressures from environmentalists,

but also partly due to the results of fundamental research, there have been more changes in stabilizers during the last 20 years than in any other aspect of PVC technology.

Historically, lead-based stabilizer systems were the first commercially successful ones for PVC. They are generally fine particle size basic solids, which disperse readily in flexible PVC compositions so that there are no significant unstabilized volume elements. Atomic chlorine and HCl released from degrading PVC, readily form basic lead chlorides which do not promote further degradation of PVC. Related theory is covered in Chapter 4.

A simple way to generalize the action of heat stabilizers in flexible PVC is the following: thermal degradation of PVC molecules starts at defect structures which may take several forms but all involve labile chlorine atoms. Unless an active stabilizer molecule is close to the site from which labile chlorine releases from PVC, a progressive “unzipping” of successive HCl molecules from the PVC is initiated. Stabilizers prevent this as follows:



Desired features for stabilizers used in flexible PVC include that they should preferably be colorless, odorless, nontoxic, tasteless, non-staining, non-volatile, nonconductive, non-extractible, non-migrating, non-plasticizing, non-plating, resistant to oxidation and hydrolysis, non-exuding, non-chalking, and non-lubricating or only weakly lubricating. They should also be low in cost, shelf stable, readily available, easily dispersed in PVC, compatible with PVC and other additives, homogeneous, heat stable, light stable, environmentally acceptable, chemically stable, easy processing, and efficient in stabilizing action.

Even though finely powdered litharge (PbO) was a fairly effective stabilizer for flexible PVC, Waldo Semon abandoned it early, because of its color, in favor of basic carbonate of white lead (BCWL). Over the years, this has been replaced by tribasic lead sulfate (TBLS), dibasic lead phthalate, and dibasic lead phosphite, all manufactured as fine white powders. TBLS has the lowest cost of these three, but is sufficiently basic to hydrolyse some polymeric plasticizers. Dibasic lead phosphite is the most expensive of the three, but is favored in some applications because it has more light-stabilizing action than TBLS or dibasic lead phthalate.

All these lead stabilizers sulfur-stain on contact with mercaptides or hydrogen sulfide. They have to be handled carefully due to their tendency to “dust”. When breathed or ingested by humans, they are slightly toxic, but only slightly so due to their low solubilities in water or saliva. They have refractive indices between 2.0 and 2.25, which are high enough to make them unusable in transparent or translucent applications due to their pigmenting action. They are among the most cost-effective stabilizers for plasticized PVC, but are generally being phased-out due to pressure from environmentalists on the PVC industry to stop using lead-containing stabilizers, pigments, or lubricants.

In the United States, problems of worker exposure to lead have been overcome by handling the powdered lead stabilizers in closed bulk air pallet systems, in pre-weighed batch charges (each in its own PVC bag), or in prilled stabilizer-lubricant one-packs. In the United States, the permissible exposure limit (PEL) for airborne lead is 0.05 mg/m<sup>3</sup> [30].

For building wire insulations for use in damp or wet locations, lead stabilizers perform the best. Many suppliers have qualified compounds, which pass long-term insulation-resistance testing. This requires immersion in water at 75 or 90 °C for twenty-six (26) or more weeks without significant loss of dielectric properties. Lead-replacement and low-lead systems continue to be actively evaluated for these uses.

TBLS and dibasic lead phthalate and dibasic lead phosphite have low solubilities in water at pH 6 to 8 (neutral). But, due to the amphoteric nature of lead, they are more soluble if the extractant is buffered to be acidic or alkaline. When lead-stabilized vinyl insulation or sheathing materials are ground to a fine particle size and subjected to EPA's Toxic Characteristic Leaching Procedure (TCLP), which is run under acidic conditions and allows a maximum lead concentration in the leachate of 5mg/l, marginal or failing results may be experienced. Therefore, lead-stabilized wire and cable PVC scrap is either recovered or sent to secure landfills, which are expensive. By contrast with lead, 100 mg/l of barium is allowed in TCLP leachates. Calcium and zinc are not regulated in this test.

Grossman has described low extractable lead stabilizers [31].

### 10.6.3 Mixed Metal Stabilizers

For many years, the most popular mixed metal stabilizers for flexible PVC were based on barium and cadmium or barium-cadmium-zinc combinations, along with various phosphites and epoxy plasticizers or resins. Cadmium has been phased out, because it is considered to be a toxicity hazard. But cadmium is present in much old flexible PVC rework. Today, many mixed metal stabilizers for flexible PVC use zinc compounds, which exchange their anions for labile chlorine atoms on PVC molecules. The zinc chloride formed in these exchanges is a potent Lewis acid capable of catalyzing catastrophic dehydrochlorination of PVC. Therefore, zinc is backed up by barium or calcium in the stabilizer at a higher level than the zinc. The barium and calcium compounds do not react with the labile chlorine atoms on PVC as actively as the zinc compounds do. Then, by anion exchange, barium or calcium chlorides are formed in the mixed metal system, and the zinc ceases to be part of a strong Lewis acid. The barium and calcium chlorides are weak Lewis acids and promote PVC degradation much less than zinc chloride does. In 1993, Baker and Grossman presented work on cadmium-free mixed metal stabilizers [32]. Today, use of cadmium has been phased out.

The barium-zinc and calcium-zinc stabilizers may be either solids or liquids. The workhorse solids consist of barium or calcium stearate, plus some zinc stearate, together with various synergists. Mixed fatty acid salts, including palmitates and laureates, are also often used. In liquid systems, barium alkyl phenates and zinc octoate may be used together, with high boiling solvents compatible with PVC. Other synergistic ingredients include epoxides and phosphite antioxidants, whose solubility parameters are close to those of PVC and other ingredients such as plasticizers in the formulation. Mixed metal stabilizers have been used for years in clear flexible PVC formulations. Alkyl aryl phosphites improve clarity and help maintain "good, early color". Pentaerythritol was found empirically to be beneficial. Phenolic antioxidants such as butylated hydroxytoluene (BHT) and Bisphenol A are included in many formulations. It is necessary to protect liquid mixed metal stabilizers from exposure to humid air by handling them in closed bulk or semi-bulk systems. Quite small amounts of water in many mixed

metal stabilizers are sufficient to cause phase separation and serious loss of properties by hydrolyzing some of the phosphite and adding to a portion of the epoxide.

Numerous calcium-zinc mixed metal stabilizers are sanctioned by FDA for use in flexible PVC food contact films. Regulated phosphites and polyols are used as synergists in these stabilizers, some of which are sold as one-pack systems. New calcium-zinc stabilizers were described by Bacaloglu [33].

The compositions of most lead-replacement stabilizers are proprietary because of unresolved patent and technical issues. They are reported to contain combinations of primary and secondary metals, metallic chloride deactivators, inorganic acid acceptors, metal coordinators, and antioxidants. Some of these use hydrotalcites similar to the well-known antacid Maalox®, which has aluminum, magnesium, hydroxyl, and carbonate functionalities.  $\beta$ -diketones, such as Rhodiastab 83® or Rhodiastab 50®, are recommended to prevent early discoloration in some lead-replacement stabilizer systems. A novel approach using “latent mercaptides” was described by Conroy [34]. Promising early work on the stabilization of PVC by “plasticizer thiols” was described by Starnes [35]. Stabilizer technology is covered in Chapter 4.

Organotin stabilizers are very successful in the United States in rigid PVC, but are only used in specialty flexible applications.

When foaming flexible PVC with azodicarbonamide blowing agents, it is advisable to use a stabilizer recommended by the blowing agent manufacturer. For satisfactory foaming, the stabilizer needs to be matched to the desired temperature range for foam formation. For instance, some lead stabilizers are good “kickers” for blowing in the range 160 to 180 °C (320 to 356 °F). Some zinc-containing stabilizers are effective kickers for blowing above 180 °C.

#### 10.6.4 Fillers

Generically, filler may be any low cost solid, liquid, or gas which occupies volume in a part and reduces its volume-cost. The flexible PVC industry uses the term “fillers” to refer to inert particulate solids incorporated into formulations for various reasons, including hardening, stiffening, and reduction of volume-cost. Functional fillers are added to improve specific properties. Examples are calcined clays added to wire insulation formulas to raise electrical volume resistivity, fumed silica or bentonite clay added to plastisols to increase their yield value, and hollow microspheres used to lower specific gravity while achieving other desired filler effects. Particulate solids called fillers must not dissolve in the flexible PVC matrix. Since many flexible vinyl products are sold by volume rather than weight, their volume-cost is the dominant economic parameter. For use in volume-cost calculations, the specific gravity of calcite is 2.71; that of true dolomite is 2.85 and that of aragonite is 2.95

The most widely used fillers in flexible and semi-rigid PVC are grades of dry-ground, wet-ground, or precipitated calcium carbonate derived from limestone or marble, which are predominantly calcite. This is the stable crystal structure of  $\text{CaCO}_3$  at ordinary temperatures and pressures. Marble consists of small, interlocking crystals of calcite. Calcite is soft, having a Mohs hardness of 3. Therefore, pure calcium carbonate fillers are low in abrasivity to processing equipment. Grades which contain significant fractions of hard silicates are much more abrasive. Recent work carried out in a PE carrier resin confirms this long-accepted fact and shows that coarser grades are more abrasive than fine particle size fillers [36].

Considerations in selecting a particular grade of calcium carbonate filler include the purity of the original ore, whether it has been dry-ground or wet-ground or precipitated, the average particle size and size distribution, and whether the particles have had a surface treatment. The “packing fraction” (PF) is a measure of how efficiently finer particles fill the voids between coarser particles. Presence of iron oxides such as  $\text{Fe}_2\text{O}_3$  in the filler tends to color a compound yellow-brown and will compromise its heat stability unless it is stabilized to withstand the presence of the iron oxide.

The average size of filler particles is usually defined in terms of an equivalent spherical diameter (esd). The ratio of the average lengths of the major to minor axes of filler particles is called the “aspect ratio”. The most used fillers have aspect ratios of less than 4 : 1. Reinforcements such as glass or metal fibers generally have aspect ratios in excess of 10 : 1.

Vinyl floor tile made by calendaring tolerates filler particle sizes up to 99% through a U.S. Standard 50 mesh screen having 297 micron openings (11.7 mils). Typical electrical insulations and cable jackets, which are extruded, require fillers with an average esd of 3 microns or less and coarsest particles of 12 microns diameter (0.47 mils). Cable jackets designed to give low HCl emission on burning generally use precipitated calcium carbonates having 0.6 micron esd. The best filler particle sizes for most flexible PVC applications are determined by experience, in optimizing end-use properties and minimizing cost.

The softest non-carbonate filler used in flexible PVC is talc represented as  $3 \text{MgO} \cdot 4 \text{SiO}_2 \cdot \text{H}_2\text{O}$ . Zero or very low content of asbestos-related minerals is specified for talcs used with PVC. Talc is often added to calendaring formulations to reduce plate-out on the rolls and to extrusion formulations to reduce plate-out on screws and dies. Talc may also be dusted at 0.1 to 0.25% onto PVC compound cubes or pellets to improve flow in bulk handling systems and hopper cars.

Mica is added to PVC compounds to impart a non-blocking surface and to provide stiffening when that is also desired. Typical grades used in non-blocking calendared films are fine-ground so that > 99% passes a 325 mesh screen (with openings of 1.7 mils or 44 microns).

Diatomite (amorphous silica) is added to PVC plastisols to increase viscosity and yield value and to reduce surface gloss after fusion. Fumed silica may be added to hot-processed compounds as a scrubbing agent and to plastisols to increase viscosity and yield value.

The refractive index (RI) of flexible PVC matrices usually ranges between 1.51 and 1.53 because the RI of PVC is 1.55 and that of typical phthalate plasticizers ranges between 1.48 and 1.50.  $\text{TiO}_2$ , with an RI of 2.76 for rutile, is a strong pigment, which contributes a high degree of opacity. Calcium carbonate (calcite), with an RI of 1.65, is a weak pigment as well as a filler for flexible PVC. Barium sulfate (Barytes), with a slightly lower RI (1.6) than calcite, may be used in translucent flexible vinyl compounds, but allowance must be made for its high specific gravity (4.5). The high gravity is an advantage for use in sound-absorbing and visco-elastic damping compounds. Clear vinyl compounds are generally unfilled.

The principal advantages of inorganic fillers in flexible PVC include cost reduction, stiffening, reducing coefficients of thermal expansion, and contributing to better flammability behavior. Specific heats per unit volume are comparable for most fillers and many polymers. The disadvantage of using high levels of fillers in flexible PVC is the reduction of tensile and tear strength, elongation at failure, toughness at low temperatures, abrasion resistance, and resistance to attack by moisture and chemicals. High filler levels also compromise processability by increasing melt viscosity.