THE GENERAL TIRE & RUBBER COMPANY
CHEMICAL/PLASTICS DIVISION • AKRON, OHIO

VYGEN®
COMPOUNDING AND PROCESSING

This information is a guide to manufacturers in the compounding and processing of Vygen resins. It clarifies the initial vinyl processing steps and the technology of plasticizers, stabilizers, pigments, fillers, and lubricants. Basic formulations for specific applications are included.

PLASTICIZERS

Molecular weight differences between PVC resins are shown in their dilute solution viscosity values. Change in molecular weight changes the processing conditions and final properties of the resin. High molecular weight resins have higher heat distortions, and generally greater strength. Their higher melt viscosity calls for hotter processing conditions. While these are important factors in a formulation, the effect of plasticizer type and amount is far greater than the effect of the resin differences. Plasticizers can be a substantial part of a flexible PVC formulation and may even equal the volume of the resin. The function of the plasticizer is to permanently soften the resin.

PVC molecules are bound along their lengths by Van der Waal forces. These forces resist slippage when stress is applied. When a plasticizer is added to hot PVC, the resin swells as the plasticizer opens the bonds. The resin is then flexible. As with most solvents, the plasticizer has a greater effect at high temperatures. The lower melt viscosity of a plasticized PVC resin permits lower, more practical processing temperatures.

The chemical structure of a plasticizer determines its compatibility, efficiency of solvation, permanence, wicking to cloth, and flame resistance in PVC resin. One plasticizer may not meet all the requirements. A blend of two or more plasticizers is often used to give a balance of properties.

The compounder may be tempted to use a highly solvating plasticizer to hold a weak plasticizer within the resin. This practice results in weak film strength. It may destroy the delicate balance of solvation through early oxidation of the plasticizer. Oxidation can cause exudation of the nonsolvent on the surfaces of the vinyl.

A number of chemicals have molecular configurations that permit their use as PVC plasticizers. The more common materials are properly engineered esters, i.e., a product of an alcohol and an acid. The polarity of an ester varies with the strength of the acid, and with the chain length and type of the hydrocarbon group of the alcohol. Highly polar tricresyl phosphate is a powerful solvent for PVC and was a common plasticizer for many years. Because it is expensive, it is seldom used today except where flame resistance is important.

Esters made from phthalic acid are commonly used plasticizers. They are moderate in cost, and can be made with sufficient polarity to give good permanence. Esters of alcohols below a chain length of eight are the better solvents but are too volatile for good permanence. The eight to twelve chain alcohols have moderately high polarity and low vapor pressure. Di- (2-ethylhexyl) phthalate (DOP) is the most common PVC plasticizer in use today. It is not a universal plasticizer because it provides only fair low temperature flexibility. It is often used in blends with octyl adipate, azelate, or sebacate to improve this property. In other applications, DOP is not resistant enough from migration into lacquers or rubber. There are polymeric plasticizers especially designed for their non-migratory properties.

STABILIZERS

Chlorinated organics tend to be unstable to heat especially where pendent chlorine and hydrogen atoms are near each other. PVC is a typical example. Hydrogen chloride is evolved when PVC is heated, turning the resin amber. It has been proposed that the loss of hydrogen chloride leads to the development of conjugated double bonds. Such molecular configurations are usually colored. This simple concept does not explain the early chain scission, subsequent chain cross linking, and serious oxidation which occur. The absence of a sound theory of the PVC decomposition mechanism has compelled the industry to develop and use vinyl stabilizers in an empirical manner.

PVC must be processed at temperatures reaching 350° F. Heat resistance during processing is therefore very important. In addition, PVC products often must maintain their initial characteristics during years of exposure to heat and light.

The rate of degradation of all grades of PVC is not constant. The resin manufacturer has considerable control over the initial stability of his product. High purity Vygen resins are of the suspension type with a narrow molecular weight range within any one grade. This is a good start, but the resin must be supported with an auxiliary stabilizer. For proper stabilizer selection, the effect of pigments, fillers, and plasticizers should be known. The processing condition is also very important in the stabilizer selection. When one formulation is being processed in different ways, the stabilizer may not be adequate for all the processes.

The complexity of resin stabilization and the lack of a full understanding of the mechanism involved has led to a large number of commercial stabilizers. Most of the available compounds do a satisfactory job in either heat or light protection when the proper stabilizer choice is made for the compound and processing condition; making this proper choice is often very difficult.

Lead compounds were the earliest PVC stabilizers used and are still the best materials for electrical insulation requiring long term, moderate heat resistance during service. The cationic lead may be associated with an anionic silicate, carbonate, basic sulfate, or phosphite as an inorganic salt. This type of stabilizer is insoluble in the plasticizer and must be thoroughly dispersed to protect the resin. Large amounts of lead salts can be used without danger of surface blooming, a hazard with large quantities of soluble stabilizers. Lead salts are opaque and cannot be used in either clear or bright colored products. They are also subject to hydrogen sulphide discoloration and should not be used in making white or pastel colored products. With other stabilizers, zinc compounds are often used to inhibit sulfur staining.

Organic salts of lead such as the stearates, phthalates, and salicylates are employed as specialty stabilizers. The stearate has limited solubility in plasticizers and is a lubricant. The amount used must be determined on the basis of both its lubricant and stabilizer properties.

Organic tin compounds were the first to replace lead. High clarity vinyl films with good light stability can be made with dibutyl tin dilaurate and dibutyl tin maleate. Tin mercaptides provide good heat stability and are used for rigid vinyls in spite of their high cost and objectionable odor.

Barium stabilizers show good long range heat stability. However, initial color of the vinyl may be greater than can be tolerated. Cadmium stabilizers provide excellent initial color and good light stability but are not recommended for long term heat stability. Some years ago it was found that a mixture of barium and cadmium organic compounds provides better stabilizing protection than either used alone. This synergistic effect was later improved by the addition of an organic phosphite to act as an antioxidant as well as a chelator (scavenger) of excessive cations. There is now widespread use of organic barium-cadmium-phosphite combinations as stabilizers for PVC.

More attention is being paid to the anion part of the compound. When stearate, laurate or other soapy radical is used, the stabilizer is simultaneously a lubricant. Excessive lubricant may lead to surface bloom or poor ink adhesion. Normally it is desirable to control the lubricant independent of the stabilizer. The phenate or octoate compounds of Ba-Cd-phosphites are often used to reduce stabilizer lubricity.

A liquid stabilizer may not be compatible with the plasticizer. If the plasticizer precipitates the stabilizer as a poorly dispersed solid, the effectiveness of the stabilizer will be impaired.

Organic compounds containing epoxide groups stabilize PVC by accepting hydrogen chloride. The epoxide group is often on a molecule that is a PVC plasticizer. A number of epoxidized soya bean oil and fatty acid esters are available that give improved light and heat stability of the vinyl.

Ultra-violet screeners have been developed to protect vinyl from sunlight. These materials are effective, but expensive.

PIGMENTATION

Fused Vygen resins are crystal clear. Optically clear products ranging from bottles to convertible rear windows can be made from them. If the pigment used in colored formulations is chemically stable under the vinyl processing procedures required, the vinyl article will be the same color as the pigment. To be stable the color pigment must resist a heat of approximately 350° F. for thirty minutes under the oxidizing and acid environment present in the vinyl compounding and converting cycle. These are severe requirements. The suitability of a pigment for vinyl applications can usually be determined from the supplier's experience.

The compounder must be sure that his clear base formulation is stable over the range of temperature-time cycles he uses. Pigment failure is often blamed when the variability in colors is due to improper stabilization.

The greatest waste in the vinyl industry is poor color standard maintenance, particularly where matching pieces are sewn together. To reduce the effect of a vary-

ing source of light and the weakness of the eye as a measuring device, the industry is using the spectrophotometer more and more as a color calibrator to maintain color standards.

Dyes are used in transparent rigid vinyl articles. Dyes are seldom used for coloring other types of PVC.

Pigments are small discrete color particles. They may be inorganic or organic. The inorganic pigments include natural and artificial "earth colors" such as the iron oxide yellows and browns. These pigments should be used with discretion. Ionic iron catalyzes PVC degradation and is potentially available in iron pigments. On the other hand, there are purified oxides which are not only stable, but are effective U.V. screening agents. Inorganic molybdate orange, lead chromate, cadmium (red, yellow and orange), titanium dioxide, bone and carbon black are used widely in the vinyl industry. The first two of these pigments are deficient in light stability and should not be used for long term service requirements.

The organic pigments are usually more expensive but are outstanding in chroma and brightness. In this class are the phthalocyanine blues and greens, pyrazolone red, and the so-called Monastral Red and Maroons. These pigments are heat and light stable in vinyl products and have high tinting strength when the pigment has been properly dispersed.

Organic pigments are obtainable as pure "toners" in which the entire color particle is made of the color molecules. They are also available as "lakes" where the color molecules have been deposited upon a colorless particle (the lake) such as aluminum hydrate. The diluted pigment on the lakes has less covering power but it does cost less and is more easily dispersed.

Organic pigments are precipitated from a water medium, washed and dried. The drying stage usually is accompanied by a formation of aggregates or clusters of pigment which are tightly cemented together. The separation (or dispersion) of the aggregates is very difficult and is seldom one hundred per cent effective. The poorer and more variable the dispersion, the greater the difficulty in color matching.

Dispersion of color is a process where the pigment agglomerates are broken into finer particles in a liquid medium. The purpose of the medium is to prevent reunion of the particles into new agglomerates. The medium must be compatible with the desired vinyl compound and is therefore usually a plasticizer. Dioctyl phthalate is often selected, although the choice is a poor one. DOP is so thin in viscosity that only weak shearing forces can be developed. More viscous mediums should be used, such as polymeric plasticizers, or a combination of DOP with a sufficient amount of dissolved PVC resin to increase the viscosity. The pigment-to-medium ratio selected should always give a firm bodied paste.

The paste is passed one or more times through a roller paint mill, ball mill, or similar grinding device that will break apart the agglomerates. When pigment is to be dispersed in PVC resin, a hot two roll mill, a Banbury, or both are used. When resin is the dispensing medium, a lower than normal temperature should be selected to increase the shearing action.

As pigments disperse, their color value and covering power increase. The degree of dispersion can be measured by "letting down" the color paste in a ratio of 1 to 20

parts of a standard titanium dioxide paste and matching against a prepared standard.

Some color manufacturers are equipped to dehydrate their "wet cake" by replacing its water content with plasticizer instead of drying. Such color pastes are known as "flush colors," and while costly, are usually well dispersed.

Separation of the medium from the pigment during storage will cause color matching problems. A heterogeneous paste is a variable color paste. Color resin chips do not phase separate. Their softening point should be low enough to mix completely into the vinyl during fluxing.

FILLERS

Unlike rubber, vinyl resins cannot be reinforced with fillers. A filler is a foreign substance physically encapsulated in the resin. Theoretically, the resin film should be weakened in a direct ratio of the relative volume of the filler to that of the resin. In plasticizer PVC, this weakening does not follow the theoretical concept exactly because the filler absorbs some plasticizer. The amount of plasticizer absorbed depends upon the filler's shape, particle size and specific surface. With less plasticizer available to the resin, the compound has a greater tensile strength. The net result of this balance of effects is that the tensile strength decreases slowly with filler additions until the quantity reaches approximately 25 parts (for calcium carbonate) per hundred of resin. More additions of filler accelerate the tensile strength loss.

Physical properties, other than tensile strength, are more rapidly affected by filler. The low temperature flexibility of a compound depends upon the quantity of plasticizer available to the resin. Loss of plasticizer to a filler increases the stiffness of the vinyl at low temperature. A compounder can partially compensate for this effect by using additional plasticizer.

With the exception of certain translucent silica and alumina fillers, most fillers are white opaque pigments. When used in large quantity, common fillers will cause loss of color, haziness, or even milkiness. Where brilliant colors are required, translucent fillers should be used.

High filler levels will cause a pigmented sheet to "whiten" during elongation. This effect may be an important factor if the goods are to be creased or folded in the fabrication or the use of the product.

Obviously, there are many limitations to consider in using fillers for vinyl. But fillers can give desirable properties to an end product. Vinyl sheeting for handbags has a dry sateen finish and leather-like hand because of a little calcium carbonate in the compound. Elimination of the filler results in a tacky, glossy product with poor hand. Calcined kaolin improves the insulation properties of vinyl used for wire and cable covering. Calcium carbonate, the most widely used filler in vinyl compounding, is an acid acceptor and mild stabilizer for inexpensive vinyl products. High concentrations of asbestos are used to make durable vinyl asbestos tile.

Proper use of fillers increases the versatility of vinyl compounds. Fillers should not be used indiscriminately. Purity is as important with fillers as with the other ingredients in the formulation. Unfortunately, excellent and poor grades of fillers are sold to the industry at price differentials that do not reflect their worth.

LUBRICANTS

A "lubricant" in vinyl terminology is in reality a parting or release agent. At processing temperatures PVC compounds tend to stick to hot metal surfaces such as the rolls of a calender. A parting agent has limited solubility in any of the components of the compound so that it exudes from the hot plastic mass. Stearic acid is an example of this type of material. When the proper amount of stearic acid is used, a microscopically thin film of the lubricant is deposited over all of the metal surfaces the hot vinyl touches during processing. The plastic is actually processed on lubricant rather than steel surfaces. The plastic produced is glossy since it parted from the forming surface without distortion. With most release agents, the parting of plastic from the steel splits the film parting agent between the separating surfaces. The plastic carries an incompatible layer of lubricant on its external surfaces. Too much lubricant film on the plastic can give poor decorative ink adhesion, or failure in dielectric sealing.

The release properties of a compound depend upon the release characteristics of all materials used and not just the lubricant. A metallic soap has definite release properties and contributes to lubrication. Plasticizers, treated fillers, and even pigments may contribute to the lubrication of the total compound.

There is a wide choice of lubricants available to the compounder. These materials are liquid or semi-liquid at processing temperatures. Fatty acids and their salts, paraffins, natural waxes, and low molecular weight polyethylene are commonly used parting agents. Stearic acid is still the most common lubricant.

PROCESSING

Preblending

In the preblending process, liquid components of a compound are absorbed into the vinyl to yield a free-flowing powder. Although a variety of equipment types are available, the basic process is the same in each.

Theory

The ingredients of a plasticized vinyl compound are a mixture of solids and liquids having limited miscibility at room temperature. In the preblending process, the resin must be partially solvated by the plasticizer. These resin particles must be dispersed thoroughly so that there is a homogeneous dissolved resin phase. Incompatible solids as pigments, fillers, or insoluble stabilizers should also be uniformly dispersed throughout the compound.

The action in the preblender is designed to distribute the plasticizer uniformly. By capillary action the plasticizer is distributed into the channels of the resin particle. Even a compound with a low plasticizer content can have uniform plasticizer distribution within the resin.

As the temperature within the blender rises, the solubility of the plasticizer for the resin increases so that resin swelling and solvation starts. As the plasticizer is absorbed within the resin particles, the mix dries. At the conclusion of the process, the compound is a dry powder with the free-flow characteristics essential for extruder feeding. Intensive action or high temperatures are not required.

Ribbon Blending

Solvation of the resin can be performed in several mixer types. The ribbon blender is one of the most popular.

The ribbon blender is a U-shaped, trough-like tank. It has closed ends and spiral ribbon agitators which scrape the sides and bottom of the trough. In the usual design, outer ribbons push the compound towards the ends of the mixer while an inner ribbon draws the compound away from the ends. The bottom section of the mixer is jacketed to permit steam heating of the mixer and its contents. Auxiliary equipment should include a pipe with spray nozzle spaced along the interior length of the tank so that plasticizer may be sprayed gradually over the agitated resin. This feed pipe may be steam lined to heat the plasticizer prior to spraying. Besides adding heat to the blender, this technique makes spraying easier; especially with high viscosity plasticizers.

The mixer is normally covered and mounted in the floor of an upper story so that it can be loaded at a workman's knee level. He can discharge the compound into equipment used for subsequent operations. A ribbon blender can prepare thousands of pounds of material to meet the demand of the processing machines.

Plasticizers vary in their solvating power. The final preblending temperature is about 180° F. when monomerics are used. Polymerics may require a 220° F. temperature or slightly higher. The dry texture of the compound will indicate whether sufficient heat has been used.

The order of addition of the ingredients of a compound to a ribbon blender depends upon the formulation. It is customary to first add the resin and filler to the blender to permit the dry solids to mix in a short time. If a low level of plasticizer is used in the compound, any filler present shares the plasticizer with the resin, thereby reducing resin solvation. Under these circumstances, the filler should be added after a dry preblend resin has been created.

The liquid or dispersed solid stabilizer should be added with the plasticizer. This addition may be made through pre-mixing the stabilizer in the plasticizer or by using a proportioning pump to feed the stabilizer dispersion into the plasticizer feed line. The liquid stabilizer should not be precipitated by the plasticizer used.

Color dispersion pastes may be added in the same manner as stabilizer dispersions. The feed line must be cleaned between different color batches. Color paste not mixed with the bulk of the plasticizer should be added to the blender immediately after completion of the plasticizer spraying, and before heating has caused the resin to become dry. This paste addition should be made in even increments. A good pre-blend is dry enough when finished to discharge without color contamination of the blender. Some colors leave a stain, necessitating cleaning the blender between different color batches.

Lubricants are highly effective in minute quantities. Processing difficulties due to either excess or insufficient lubricant may be caused by a weighing inaccuracy or variable distribution. The same difficulty occurs with lubricating stabilizers. Lubricants should be pre-dispersed in the color paste, or melted and mixed in a portion of the plasticizer. These methods make dispersion of the lubricant easier.

Intensive Mixers

Several brands of vinyl preblenders on the market operate on a principle of high shear and intensive mixing action. The main advantage of these high shear mixers is the short time cycle required. In very low plasticizer compounds or rigid vinyl formulations, high shear may be necessary to give adequate mixing. Heat is sup-

plied in the mixer by frictional forces. Cooling of the batch is usually done in a ribbon blender in a subsequent operation.

Fusion

In the preblend, the partially solvated resin consists of discrete particles slightly larger than the initial resin. The second step in creating a homogeneous mix calls for increasing the solvating power of the plasticizer by heat, and reducing the swollen resin particles to molecular dimensions through intensive shear. This step is usually done in a Banbury or on a mill.

Banbury

The most common production equipment for intense shearing of compound is a high speed, controlled temperature machine known as a Banbury. This mixer consists of a chamber (stator) which holds the compound while it is masticated by a rotating sigma blade (rotor) turning within the stator. Both the rotor and stator are water cooled to control the temperature of the compound. The cycle for the fusion and dispersion is about four to five minutes. The weight of the batch varies between 100 and 700 lbs., depending on the specific gravity of the vinyl compound and the capacity of the Banbury used. Upon completion of the Banbury operation, the mass is homogeneous and in the ideal rheological condition to convert into the final product.

Mills

When compound demand is less than the capacity of a Banbury, the preblended compound may be homogenized by shearing it between two heated rolls. Similar two roll mills are used for rubber compounding. Vinyl mills are modified in the bearing design to permit high temperature operation (up to 400° F.). The rolls have a differential in speed so that powder compound fed between the "bite" of the rolls is sheared. The rolls add heat as well as work to the compound. Conversion to the plastic state on a mill is similar to Banbury operation, although a mill is considerably less efficient in shear and capacity.

One or more mills are often used after a Banbury to remove entrapped volatiles. A mill can be used as a reservoir of vinyl for continuous feeding to the converting machine, thereby evening out the intermittent flow of material from a Banbury cycle.

A mill can be used to produce granulated compound. By closing the clearance between the rolls the two roll mill produces a thin band of plastic. A vinyl strip can be continuously cut from the rolls, cooled, and diced into granules or pellets for subsequent feeding to an extruder.

Converting

Compounding and mixing processes are only preparatory operations for conversion of the vinyl into the final article. Vinyl compounds can be calendered, extruded, compression injected or blow molded into a wide variety of shapes and forms. Vinyl converting equipment originally was adapted from similar rubber machinery. The equipment developments in this area have progressed far beyond the original simple rubber forming devices. Vinyl converting is too complex to be treated in this brief discussion. Our service engineers are always available for advice and instruction in specific problems in conversion.

SUGGESTED BASIC FORMULATIONS

General Purpose Film

Vygen 110	100.0
DNOP	45.0-50.0
Epoxy plasticizer	3.0-5.0
Stearic acid	0.2
Liquid barium — cadmium stabilizer	1.5-2.0

Low Cost Film

Vygen 110	100.0
DOP	50.0-55.0
Epoxy plasticizer	3.0-5.0
Aluminum hydrate	10.0
Stearic acid	0.2
Liquid barium — cadmium stabilizer	2.0

Drapery Film

Vygen 110	100.0
Isooctyldecyl phthalate	20.0
DOP	30.0-35.0
Epoxy plasticizer	3.0-5.0
Stearic acid	0.2
Liquid barium — cadmium — zinc — chelator stabilizer	1.5-2.0

Calendered Sheeting — Handbag

Vygen 110	100.0
DOP	43.0
Chlorinated paraffin	7.5
Calcium carbonate filler	25.0
Lead stabilizer	4.0
Stearic acid	0.25

Calendered Sheeting — Handbag

Vygen 110	100.0
DOP	30.0
DDP	24.0
Calcium carbonate filler	38.0
Epoxy plasticizer	3.0
Liquid barium — cadmium stabilizer	1.5
Liquid zinc stabilizer	0.5
Stearic acid	0.25

0.012" Unsupported Sheeting

Vygen 110	100.0
DOP	40.0-50.0
Epoxy plasticizer	3.0
Calcium carbonate filler	15.0
Barium — cadmium — chelator stabilizer	2.0
Stearic acid	0.25

0.020" Unsupported Sheeting

Vygen 110	100.0
DOP	55.0-60.0
Epoxy plasticizer	3.0-5.0
Calcium carbonate filler	15.0
Barium — cadmium — chelator stabilizer	1.5-2.0
Stearic acid	0.25

Luggage Coated Fabric

Vygen 110	100.0
DOP	60.0
Epoxy plasticizer	5.0
Calcium carbonate filler	10.0
Barium — cadmium — zinc stabilizer	2.0
Stearic acid	0.25

Upholstery Coated Fabric

Vygen 110	100.0
DOP	45.0-65.0
Epoxy plasticizer (soya-bean oil type)	5.0
Calcium carbonate filler	25.0
Barium — cadmium stabilizer (chelator — 0.5 or) (zinc stabilizer — 0.30)	2.0
Stearic acid	0.25

Automotive Coated Fabric

Vygen 110	100.0
DOP (or straight chain octyl phthalate)	40.0-50.0
Low temperature plasticizer	25.0-30.0
Monomeric epoxy plasticizer	5.0
Calcium carbonate filler	25.0
Barium — cadmium — zinc stabilizer	2.5
Stearic acid	0.25

Extruded Refrigerator Gasket

Vygen 120	100.0
Epoxy plasticizer	3.0-5.0
Polymeric plasticizer	80.0-90.0
Calcium carbonate	50.0
Barium — cadmium soap — chelator stabilizer	2.0-2.5
Processing wax	0.25

Extruded Shoe Welting

Vygen 120	100.0
DOP or DNOP	50.0
Epoxy plasticizer	5.0
Calcium carbonate	15.0
Liquid barium — cadmium — zinc stabilizer	2.0-2.5
Processing wax	0.2

Extruded Cl ar Garden Hose

Vygen 120	100.0
DOP or DNOP	45.0
Epoxy plasticizer	5.0
Liquid barium — cadmium — chelator stabilizer	1.5-2.0
Stearic acid	0.3
Mineral oil	0.3

Extruded Clear Garden Hose

Vygen 120	100.0
DOP or DNOP	30.0
Epoxy plasticizer octyl epoxy stearate or tallate	20.0
Liquid barium — cadmium — chelator stabilizer	1.5-2.0
Stearic acid	0.3
Mineral oil	0.3

Opaque Garden Hose

Vygen 120	100.0
DOP	45.0-50.0
DOA or octyl epoxy stearate	10.0
Calcium carbonate	25.0
Epoxided soya bean oil plasticizer (used with DOA)	5.0
Barium cadmium stabilizer	2.5
Stearic acid	0.3
Mineral oil	0.3

Injection Molding Compound

Vygen 85	100.0
DOP	40.0
Polymeric plasticizer	40.0-50.0
Calcium carbonate	30.0
Lead stabilizer (or cadmium-barium-zinc liquid stabilizer-2.5)	8.0
Fused lead stearate	1.0
Processing wax	1.0

Injection Molding Compound

Vygen 85	100.0
Epoxy plasticizer	5.0
Di-n-ODP	70.0-80.0
Calcium carbonate	25.0
Lead stabilizer	8.0
Fused lead stearate	1.0
Processing wax	0.5