HANDBOOK OF VINYL FORMULATING

SECOND EDITION

Edited by

Richard F. Grossman

WILEY-
INTERSCIENCE

A JOHN WILEY & SONS, INC., PUBLICATION

HANDBOOK OF VINYL FORMULATING

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PREFACE TO THE SECOND EDITION

As Ed Wickson stated in the Preface to the First Edition, the *Handbook of Vinyl Formulating* is the only text devoted to that topic. It has been highly successful; copies are in the hands of most of the vinyl technologists in North America and many throughout the world. Vinyl formulating has developed considerably in a number of areas since 1993. The Second Edition addresses these developments.

Certain of the chapters of the First Edition have been combined. “Antidegradants,” for example, covers antioxidants, heat stabilizers, light stabilizers and biocides. The reason is that, in formulating, the technologist must consider all of these in developing a stabilization package. Presentation in a single chapter enables correlation without repetition. Similarly, “Fillers and Reinforcements” combines several chapters. The technologist is encouraged not to look at individual ingredients but to look at all in a given class, to experiment with several and, when needed, to innovate useful blends. To this end, suggestions are included regarding experiments that have not as yet been reported but that seem interesting.

There has been a conscious effort to avoid material better suited to more specialized texts in order to concentrate on formulation. This does not include rationalization as to why ingredients have the effects observed, since such theorizing is vital to innovation. Another factor important in product development is intellectual satisfaction. To that end, authors and editor have done their best not to be boring.

Richard F. Grossman

Wilmington, DE

PREFACE TO THE FIRST EDITION

Although superseded by polyethylene as the world's number one plastic, polyvinyl chloride (PVC) retains its title as the most versatile of all plastics—both in the number of ways it can be processed and in the range of end products. This is due to (a) the wide variety of PVC resin types available (varying in molecular weight and distribution, homo-, co-, and terpolymers, particle size and distribution, morphology, crystallinity, etc.) and (b) the ability of PVC to be formulated with a multitude of additives, unmatched by any other plastic.

There is a wealth of information on PVC technology available in various scientific and trade journals, proceedings of technical meetings, and technical literature of suppliers of PVC resins and additives. There are also several excellent books on the broad aspects of PVC technology and on additives for plastics. However, none focuses on PVC formulating. This volume is the end result of what the editor had long felt was a need for a one-volume, ready-reference book describing in detail the properties of the various commercial PVC resins available in the United States and Canada and how these, together with additives, are used in formulating PVC. Related chapters cover economics of formulating, basic statistics and design of experiments, laboratory compounding and test methods, and environmental and health concerns in formulating vinyl compounds. Although emphasis is on formulating in this book, separate chapters are also included on dry blending, powder coatings, plastisol and organosol preparation, and electron beam radiation curing because these are not all covered in currently available books.

Because of its complexity, there is probably no one person who could claim to be truly expert on all aspects of the resins and additives used in PVC formulating. With this in mind, the editor chose experts well qualified in their particular field to author the various chapters. The reader is encouraged to contact these experts for additional information.

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Special thanks are due my wife, Ann, for help and encouragement, including surrendering the living room during the preparation of the manuscript.

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Baton Rouge, LA
March 1993

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CHAPTER 1

Formulation Development

EDWARD J. WICKSON and RICHARD F. GROSSMAN

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1.1 INTRODUCTION

Polyvinyl chloride (PVC, vinyl) became a major factor in commercial manufacture of flexible goods after World War II, replacing rubber, leather, and cellulosics in many areas. As processing technology developed, unplasticized (rigid) PVC began expansion into replacement of metal, glass, and wood, a trend that continues and which now consumes the greatest part of PVC usage. The acceptance of PVC is based on its performance-to-cost ratio. A broad range of useful properties, such as stability, weatherability, inertness to many media, and inherent flame and microbial resistance, are available, with proper formulating, at low cost.

PVC is the thermoplastic polymer most easily varied in properties through formulation. Filler levels vary from a few parts per 100 of resin (phr) in pressure pipe to hundreds of phr in extruded cove base or calendered floor tile. The latter could reasonably be described, based on the most prevalent ingredient, as marble rather than vinyl flooring. In other applications, plasticizer levels as high as 70 phr are common. PVC compounds invariably contain heat stabilizers and lubricants (or ingredients that do both). They may contain fillers, plasticizers, pigments, antioxidants, biocides, flame retardants, antistatic agents, impact modifiers, processing aids, and other

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ingredients, including other polymers. Formulation is therefore complex. The goal of this text is to make the process easier to understand and carry out.

1.2 EFFECTS OF FORMULATION ON PROCESSING

The aim of the formulator should be to develop a robust compound, that is, one that will process satisfactorily and yield acceptable properties even if processing or service conditions deviate from those anticipated or thought ideal. This must be done within certain cost parameters. Therefore, the goal, in practice, is to develop the best compound that the application can afford. This should be considered rational formulating. The alternative—development of the lowest-cost compound that can possibly be processed or manage to conform to expectations in testing or service—usually creates more problems than it solves. Although this text is directed primarily to the formulator of rational compounds, it is anticipated that others, radically constrained by cost considerations, may find guidance as well.

The formulation that is optimum today may not be so next year. If it is optimum in one plant, even on one processing line, it may be less so on another. The adaptability of PVC to various processing techniques is stimulation to the ingenuity of the plastics engineer. PVC compounds are calendered, extruded, molded by various techniques, coated, and cast. In these applications, processing begins with a blending step in which additives are mixed with PVC resin. The result may be a (more or less) dry blend, plastisol, organosol, blended latex, or solution. The blending step is followed by fluxing and fusion in the product-forming step (usually the case with rigid PVC) or in a separate pellet-forming step prior to product manufacture. The latter is common with plasticized (flexible) PVC, particularly if the pelletized compound is to be transported to another location, for example, the factory of a customer.

The rate of dry blending can be of concern if it is output-limiting. Although this may be affected by a number of ingredients, it is primarily dependent on the PVC resin and particular plasticizer. Certain resins are designed for rapid plasticizer uptake. Plasticizer type (polarity), viscosity, and solvent power are key factors. These, however, are usually determined by the application rather than ease of incorporation. Typically, processing is adjusted to suit the formulation, by such steps as preheating the plasticizer and following a judicious order of addition of ingredients. Dry blending and blending of solution vinyl, latexes, plastisols, and organosols are discussed in specific chapters of this book.

The resin is of key importance, whether fluxing rigid or flexible compositions. Examples of fast-fluxing resins include low-molecular-weight (low *K*-value) homopolymers and vinyl acetate copolymers. Plasticizers that are strongly solvating, such as butyl benzyl phthalate (BBP), increase flux rate. Again, the selection of both resin and plasticizer is usually dictated by the application. Therefore, the choice of other ingredients, particularly lubricants, stabilizers, and processing aids, is used to increase or decrease the rate of fusion.

In large-volume rigid PVC applications, dry blend is used directly to manufacture articles such as pipe, siding, and window profiles. Certain high-volume flexible applications, such as extrusion of wire coverings, are also often run from dry blend. Most flexible compounds are, however, fluxed and pelletized, using the combination of an internal batch mixer and a pelletizing extruder, an extruder that can do both, or a combination of extruders. In melt processing, viscosity and friction with metal surfaces are not only obvious factors needed for fusion and pellet formation, but also limitations of output, causes of equipment wear, and potential sources of PVC degradation. This, of course, is also the case with processing to form specific articles. All of the above are influenced critically by formulation and by selection of processing equipment. The extremes of the interaction of formulation and processing in the thought processes of formulators are as follows:

1. The optimum compound having the best available properties-to-cost ratio is developed. Then processing equipment yielding the greatest output and consistency is put into place and duplicated as new facilities are built. This scenario is the case with most high-volume rigid PVC applications and underlies the rapid growth of this sector in North America. A consequence is that suppliers of equipment and of ingredients are driven to cooperate by development of new and improved products.
2. At the other extreme, formulation is continued, often endlessly, to generate compounds that manage to conform to product expectations after on-the-edge processing, using a variety of equipment that happens to be on hand, or that may be obtained at the lowest investment. This is the case with certain flexible PVC applications. It is an important cause of market share decline from offshore competition and displacement of PVC by newer systems, for example, by thermoplastic elastomers.

1.3 EFFECTS OF FORMULATION ON PROPERTIES

In unplasticized compounds, structural rigidity (flexural strength) increases with increasing molecular weight (MW). Up to a point, filler addition increases flexural strength, while impact modifiers and processing aids tend to cause a decrease unless they also function as heat distortion improvers.

Tensile strength, on the other hand, tends to level off as MW is increased, although low extension modulus parallels flexural strength. Abrasion and creep resistance, as with plastics generally, increase with increasing MW, as does cut through resistance. Filler addition can improve both properties to the extent to which particle size and shape create structure in the composition.

Chemical and oil resistance also improve with increasing MW, as does resistance to heat distortion. The attributes that decline with increasing MW are, of course, output and ease of processing. Thus, formulation includes the use of additives that improve the flow of compositions based on high-MW resin, and those that tend to compensate for the choice of a lower-MW alternative. It has, in fact, been suggested that a key purpose of additives is to correct problems introduced by other additives.[1]

Compounds containing about 25 phr active plasticizer, such as di-2-ethylhexyl phthalate (DOP:100 percent tensile modulus about 3300 psi) are considered semirigid. Low extension tensile modulus is a reasonable measure of the flexibility of plasticized PVC. It increases somewhat with increasing MW and decreases strongly with increasing plasticizer content. Above about 35 phr DOP, or plasticizer with comparable activity, PVC is considered flexible. At 50 phr, 100% tensile modulus has dropped to about 1700 psi, and at 85 phr, about 650 psi, indicating a highly flexible compound. Lower levels of a more efficient plasticizer will generate comparable data, while less efficient ones would have to be used at higher levels. In plasticized compounds, tensile strength increases more or less linearly with increasing resin MW. Plasticizer type and level have a more profound effect. Both tensile strength and elongation often, but not always, decrease with increasing filler level. Tear strength improves with increasing MW, as does abrasion resistance, but these also depend on the effects of additives. Copolymerization with vinyl acetate leads to similar effects as plasticizer addition, often with fewer associated side effects, but usually at higher cost.

The major factors affecting low-temperature brittleness and flexibility are the level and type of plasticizer. Compounds for low-temperature service most often use blends of standard with special-purpose low-temperature plasticizers (e.g., di-2-ethylhexyl adipate (DOA)). Plasticization typically decreases chemical, solvent, and oil resistance. This can be countered by use of polymeric plasticizers, with attendant increase in cost and typical loss of processing ease, or by means of blends and alloys with highly oil-resistant polymers such as acrylonitrile–butadiene rubber (NBR).

One of the major uses of flexible PVC is in wire coverings. The service rating determines the choice of plasticizer, chosen so as to resist volatilization during the heat aging tests needed to qualify. Loss of plasticizer is the major cause of decreased elongation after heat aging. For service in dry locations, most such compounds use calcium carbonate ($CaCO_3$) filler. The level is adjusted to balance material cost versus requirements such as abrasion and cut through resistance. Insulations for service in wet locations, where testing (in North America) requires stable volume resistivity for 6 months in 75 °C or 90 °C water, are best served instead with electrical grades of calcined clay. For such service, the plasticizer and other ingredients must be electrical grades. Long-term wet electrical requirements necessitate close quality control of all materials.

Plasticized PVC compounds can have flame resistance ranging from slow-burning, when flammable plasticizers are used, to self-extinguishing when compounded with the halogen synergist antimony oxide, flame-retardant plasticizers, and hydrous fillers such as aluminum trihydrate (ATH) or magnesium hydroxide. Although hydrous fillers add to heat stability, flame-retardant (FR) plasticizers usually require higher levels of stabilizer. Hydrous fillers also reduce smoke generation by promoting oxidation of hot carbon particles (water gas reaction). This reaction is thought to go through metal carbonyl intermediates and is catalyzed by compounds of metals that form carbonyls. The most commonly used is molybdenum, in the form of ammonium octamolybdate (AOM), which reacts at useful temperatures. Flame resistance is increased and smoke generation decreased by fillers that promote formation of a thermally conductive glassy char during combustion. These include hydrous fillers and certain zinc compounds, notably zinc borate and hydroxystannate. The use of zinc compounds typically requires higher stabilizer levels. This is not the case with antimony oxide, but its use increases smoke generation. Thus, the compounding of highly FR flexible PVC requires complex balancing of ingredients. The overall balance of physical and FR properties of suitably compounded FR flexible PVC is very much better than that of "halogen-free" polyolefin substitutes. The latter typically are so overextended with hydrous fillers that the polymer is no more than a binder.

Rigid PVC foamed composites, consisting of solid layers above and below a foam core, have become increasingly accepted in pipe, siding, and plastic lumber. In addition to weight and cost reduction, thermal conductivity of vinyl siding is decreased, and lumber products are more readily nailed or sawn. Flexible PVC foamed products are most often run from plastisols, as in continuous vinyl flooring, and may be made mechanically by introducing air with strong agitation, or chemically with blowing agents, most often azodicarbonamide. The latter is readily activated by a number of additives, often components of the heat stabilizer, known in such cases by the jargon "kicker." Surfactants are used to improve cell structure quality, which is also dependent on resin and plasticizer choice.

Light stability and weatherability are provided in a number of ways. The outer layer (topcoat) of vinyl siding or window profile will contain sufficient titanium dioxide (TiO_2) of a suitable grade. Its high dielectric constant enables absorption of a quantum of light and dissipation of energy as heat before a lower-energy photon is emitted. This limits the extent to which incident light is capable of initiating chain reaction free-radical oxidation. Carbon black, again of suitable grades, has the same effect and is widely used in cable jackets and agricultural sheeting. It is, of course, useful to have products that are other than white, black, or gray. Pigments that behave similarly to TiO_2 are used in vinyl siding provided in colors. Other strategies include use of light-resistant topcoats such as acrylics and polyvinyl difluoride (PVDF) over a PVC substrate. Acrylic coatings are also used over PVC plastisol impregnated polyester mesh in flexible signage backgrounds to provide improved printability and resistance to plasticizer migration as well as light stability. In such cases and in other clear and brightly colored products, organic ultraviolet (UV) light absorbers are included. These function in an analogous manner to carbon black and TiO_2. A photon of light is absorbed, driving the UV light absorber into an excited state. The latter is resonance-stabilized and persists long enough to dissipate energy as (more or less) harmless heat. Additives that are strictly light absorbers, such as hydroxybenzophenones and benzotriazoles, are not antioxidants—in fact, they require antioxidant protection. A newer class of materials, hindered amine light stabilizers (HALS), are not only antioxidants but participants in a chain-reaction antioxidant action. The use of HALS in PVC is now in exploratory stages.

Weatherability of PVC compounds is studied in a variety of devices that simulate sunlight. There is only relative correlation between these methods and actual outdoor exposure. The effects of outdoor exposure itself vary from location to location. There is even suspicion that accelerating outdoor aging using magnification of sunlight introduces variability. Nevertheless, these methods are useful in comparing one compound with another, and the results are often thought predictive of field service by product manufacturers. Field service in plasticized compounds is also prejudiced by microbial attack in humid locations. Since it is often impossible to predict service conditions, the use of biocides in flexible compounds is common.

The mixing of particulate and low-MW ingredients into polymeric compositions leads one to consider the conditions under which they might overcome the entropy gain of mixing, that is, unmix. This can occur in both dynamic and static situations. In turbulent flow, the lowest-energy state is often stratification rather than homogeneity. Deviation from streamline flow in processing equipment, if severe enough, can cause partial fractionation of compounds. This is a driving force leading to plateout on equipment surfaces and deposition of ingredients on extruder screens. The rate of separation from a mixture (the instability of a phase) is a function of the density of the ingredient. Thus, the ingredient found first on the screenpack is the lead stabilizer or its reaction product, or (in otherwise stabilized compositions) titanium or zinc. If barium is present in the stabilizer, it is typically the ingredient that must be protected from plateout. Turbulent flow cannot be completely avoided. It is, in fact, a desirable feature of mixing because of its action in breaking up agglomerates (filler dispersion). It should, however, be minimized during product formation. This will aid in formulating towards the best possible cost-to-properties ratio.

A second area of concern is whether ingredients will stay put during service. Surface oxidation of siding or profile, for example, may cause a case-hardening effect through crosslinking. The result of the resultant increased surface modulus is to make inclusions less compatible, leading to "chalking," generally of the most dense species, TiO_2. This may or may not be thought desirable. In flexible PVC, plasticizer remains homogeneously distributed (except under severe turbulent flow) because of dipole–dipole attraction to the polymer. But will this be the case if an object having high plasticizer solubility, such as polystyrene or a pressure-sensitive adhesive, is in contact with the plasticized PVC article? Migration can be minimized by formulation with polymeric plasticizers, as in refrigerator gaskets and pressure-sensitive tapes, or by use of NBR or ethylene vinyl acetate (EVA) alloys to achieve flexibility. The plasticizer may carry other ingredients to the surface, which can contribute to taste and odor from food packaging film, bottle cap liners, or refrigerator parts. Occasionally, this feature is put to good use, as in self-cleaning flooring topcoats, where the plasticizer is chosen to have slight outward migratory tendency, limiting the penetration and facilitating the removal of oily dirt.

Plasticizer migration is also a concern in medical and food packaging applications. Despite the migratory potential of DOP in medical devices and of DOA and DOP in food packaging applications, the history of safe usage, low cost, and expense of obtaining regulatory approval have worked against the adoption of technically more suitable plasticizers. These are some of the most common questions encountered with the invention of a new or improved ingredient:

- Will its use be cost-effective?
- Can long-range service performance be assured?
- Can approvals be secured?

The last of these is a reminder that effective formulation cannot be carried out in a vacuum. There must be input from and cooperation by all departments of the prospective supplier of a new additive.

The above generalizations are admittedly oversimplified and will be amplified in the chapters to follow.

1.4 COMPOUND DEVELOPMENT PROCEDURE

If the application in mind is new or a new use, it is necessary to make sure that dated records of formulation development and testing are kept, in light of potential patentability. If there are similar products in the field, their advantages and limitations must be considered. One should list the characteristics that would be ideal (sometimes they may be within reach) and discuss with marketing what considerations would lead to acceptance of the product. One should, further, consider the relation between the project in mind and others that have been worked on, and work by others of which one is aware. Consideration before plunging in can be very valuable. It is often possible to make an educated guess as to the most promising solution before beginning experimentation. These steps are part of design of experiments, even though difficult to formalize.

This should be followed by a review of specifications for the product. These include not only documents from regulatory agencies, but also statements of customer requirements or samples of competitive articles. One should be sure that test methods are specified in adequate detail. In some instances, starting-point formulations can be taken from suppliers' literature (or sources such as this text). Ingredient suppliers are often willing to cooperate in a program of testing. On the other hand, there are applications in which the formulator desires to have as little outside awareness of the program as possible. This must be balanced against the fact that with modern analytical equipment and sufficient effort, all compositions can be reconstructed.

At this point, a program of experimentation can be designed, either informally (which is usually the case when the general area is well known) or statistically (which is common when one is at the edge of known technology). In the most common instance, the actual experimental work is likely to be carried out by a technician (while the investigator is involved in nontechnical tasks). The instructions to the technician should indicate the most likely outcome of the experiments, so that unexpected results can be appreciated and reported promptly. It is with the unexpected that we learn. The successful innovator follows Pasteur's dictum that chance favors the well prepared. To make such observations, it is, of course, better to run the experiments oneself (except in cases where one anticipates that the technician will do more careful work).

One should record mixing conditions where possible, noting time–temperature characteristics of the blending and fluxing stages. These can be checked versus running the same composition in a torque rheometer. Full fusion is necessary if original and heat-aged physical properties are to be meaningful. When obtaining tensile data, particularly in comparison with control or competitive samples, it is best to run the entire stress–strain curve rather than noting merely data at break or yield points. The experienced chemist can deduce differences in formulation from characteristics of the shape of such curves. If a sample shows a major excursion from average data, it is useful to try to determine the reason. For example, an unusually poor value for tensile strength combined with more or less normal 100 percent modulus is a clue to search the sample break for undispersed ingredients. (An unusually high value of tensile strength would of course be more provocative.)

Finally, one should examine the results of every program of experimentation to determine whether they would instead, or in addition, apply well to some other problem of interest—perhaps one that refused facile solution in the recent past.

1.5 COST OF INGREDIENTS

Although a few ingredients (e.g., hydrocarbon oils) are sold by volume, most are purchased by weight, as is custom-mixed compound. On the other hand, vinyl articles are sold on a volume basis. Thus, materials cost must also be known per standard volume. Throughout most of the world, this is the liter. The formula weights (kg) of ingredients are divided by their densities to yield volumes of each. The total volume and total weight ratio yields the calculated (or theoretical) density of the composition. In the United States, it is common to express recipe weights in lbs. The associated volume is the lb/volume. It is most often calculated by divided the formula weight by the specific gravity, the ratio of its density to that of pure water at a given temperature. Specific gravity (SpG) is therefore dimensionless, and lb/volume (or kg/volume) merely a construct. Since the difference between density and SpG is typically small, the calculations remain meaningful.

In unplasticized PVC, calculated SpG should compare quite closely to that measured on the finished article. Deviations on the low side suggest porosity or incomplete fusion and, therefore, make the observation well worthwhile. If, on the other hand, a foamed structure is intended, the measurement is even more significant. Plasticized PVC articles should have a SpG slightly higher than that calculated, depending on the level of plasticizer. This is a solvation effect that is well known.[2] If there is no such effect, that is, there is a substantial plasticizer level but complete agreement (to 0.001) between observed and calculated SpG, one should (after repeating the calculation) check thoroughly for plasticizer migration tendency. In general, one should check SpG routinely as an estimate of correct formulation before spending time with physical testing. A corollary is to check mass balance periodically, that is, to check that the decrease in inventory of resin and other ingredients corresponds to the quantity of compound produced.

Plasticizer loss can occur through volatilization during processing, particularly during fusion of plastisol coatings. Here losses can be in the range of several percent. This may be unavoidable because of product requirements, but must be considered in cost calculations, and in design of pollution controls. To assist in cost calculations, the specific gravities of common ingredients have been listed in the following section.

TABLE 1.1 Specific Gravity of Polymeric Ingredients

PVC homopolymer	1.40
PVC/vinyl acetate (VA), 2% VA	1.39
PVC/VA, 5% VA	1.38
PVC/VA, 10% VA	1.37
PVC/VA, 15% VA	1.35
Acrylic impact modifier	1.10
Acrylic processing aid	1.18
Acrylonitrile butadiene styrene (ABS) impact modifier	0.95–1.04
Methacrylate butadiene styrene (MBS) impact modifier	1.0
Poly(α-methylstyrene)	1.07
Chlorinated polyethylene (CPE), 42% Cl	1.23
Chlorosulfonated polyethylene (CSM)	1.18
NBR, medium acrylonitrile (ACN)	0.99
PVC/polyurethane (PU) blends	1.3–1.4

1.6 SPECIFIC GRAVITY OF INGREDIENTS

SpG of polymeric ingredients is given in Table 1.1. SpG of phthalate plasticizers is given in Table 1.2, that of speciality plasticizers in Table 1.3, and that of miscellaneous plasticizers in Table 1.4. SpG of commonly used organic additives is given in Table 1.5 and that of inorganic additives in Table 1.6.

TABLE 1.2 Specific Gravity of Phthalate Plasticizers

Dibutyl (DBP)	1.049
Diisobutyl (DIBP)	1.042
Butyl octyl (BOP)	~1.0
Dihexyl (DHP)	1.007
Butyl benzyl (BBP)	1.121
Dicyclohexyl (DCHP)	1.23
Di-2-ethylhexyl (DOP)	0.986
Diisooctyl (DIOP)	0.985
Dicapryl (DCP)	0.973
Diisononyl (DINP)	0.972
Di-trimethylhexyl	0.971
C_9 linear	0.969
Diisodecyl (DIDP)	0.968
C_7–C_9 linear	0.973
n-C_6–C_{10} (610P)	0.976
n-C_8–C_{10} (810P)	0.971
C_{11} linear (DUP)	0.954
Undecyl dodecyl (UDP)	0.959
Ditridecyl (DTDP)	0.953

TABLE 1.3 Specific Gravity of Specialty Plasticizers

Di-2-ethylhexyl adipate (DOA)	0.927
Diisooctyl adipate (DIOA)	0.928
Diisodecyl adipate (DIDA)	0.918
n-C_6–C_{10} adipate (610A)	0.922
n-C_8–C_{10} adipate (810A)	0.919
Di-n-hexyl azelate (DNHZ)	0.927
Di-2-ethylhexyl azelate (DOZ)	0.918
Diisooctyl azelate (DIOZ)	0.917
Dibutyl sebacate (DBS)	0.936
Di-2-ethylhexyl sebacate (DOS)	0.915
Diisooctyl sebacate (DIOS)	0.915
Tri-2-ethylhexyl trimellitate (TOTM)	0.991
Triisooctyl trimellitate (TIOTM)	0.991
n-C_8–C_{10} trimellitate (NODTM)	0.978
Triisononyl trimellitate (TINTM)	0.977
2-Ethylhexyl epoxytallate	0.922
Epoxidized soybean oil	0.996
Epoxidized linseed oil	1.034

TABLE 1.4 Specific Gravity of Miscellaneous Plasticizers

Tricresyl phosphate (TCP)	1.168
Tri-2-ethylhexyl phosphate	0.936
Ethylhexyl diphenyl phosphate	1.093
Isodecyl diphenyl phosphate	1.072
Isopropyl diphenyl phosphate	1.16–1.18
Acetyl tributyl citrate	1.05
Chlorinated paraffin, 42% Cl	1.16
Di-2-ethylhexyl isophthalate (DOIP)	0.984
Di-2-ethylhexyl terephthalate (DOTP)	0.984
Dipropylene glycol dibenzoate	1.133
Isodecyl benzoate	0.95
Propylene glycol dibenzoate	1.15
Hercoflex® 707	1.02
Nuoplaz® 1046	1.02
Trimethyl pentanediol diisobutyrate (TXIB)	0.945
Polyester, low MW	1.01–1.09
Polyester, medium MW	1.04–1.11
Polyester, high MW	1.06–1.15
Naphthenic oil	0.86–0.89
Alkyl phenyl sulfonate	1.06

TABLE 1.5 Specific Gravity of Organic Additives

Ethylene bis(stearamide) (EBS)	0.97
Calcium stearate	1.03
Glycerol monostrearate (GMS)	0.97
Paraffin wax	0.92
Low-MW polyethylene (PE) wax	0.92
Oxidized PE wax (OPE)	0.96
Mineral oil	0.87
Stearic acid	0.88
Bisphenol A	1.20
Topanol® CA	1.01
Irganox® 1010	1.15
Irganox® 1076	1.02
Benzophenione UV light absorbers	1.1–1.4
Benzotriazole UV light absorbers	1.2–1.4
Hindered amine light stabilizers (HALS)	1.0–1.2

TABLE 1.6 Specific Gravity of Inorganic Additives

Calcium carbonate	2.71
Talc	2.79
Calcined clay	2.68
Barytes	4.47
Mica	2.75
Alumina trihydrate (ATH)	2.42
Antimony trioxide	5.5
Antimony pentoxide	3.8
Magnesium hydroxide	2.4
Basic magnesium carbonate	2.5
Molybdenum oxide	4.7
Zinc borate	2.6
Carbon black	1.8
Titanium dioxide	3.7–4.2

1.7 DESIGN OF EXPERIMENTS

Experimentation has two general goals: an improved understanding of how and why effects occur, generally thought of as mechanism; and development or improvement of specific products and processes. Despite human attempts, the goals are inseparable. Understanding of the underlying physics and chemistry aids in problem-solving as surely as experimental results create and modify theoretical explanations. The vinyl formulator is urged to continue to read in the basic sciences and further, to proceed now to Chapter 22 for an expert's discussion of how to mechanize problem-solving.

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CHAPTER 2

Resin Selection for PVC Applications

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2.1 INTRODUCTION

2.1.1 An Extremely Brief History of PVC

Vinyl chloride monomer (VCM) is believed to have been synthesized for the first time by Regnault in 1838. Regnault may have also been the first person to polymerize VCM when he noted that test tubes containing VCM formed a white powder when exposed to sunlight. The earliest recorded polymerization of VCM yielding polyvinyl chloride (PVC) was by Baumann in 1872.[1] The first scientists who attempted to examine the thermoplastic characteristics of PVC quickly discovered its annoying tendency to evolve hydrogen chloride when heated. Because of this, PVC was little more than a laboratory curiosity up through the early part of the 20th century.

The discovery of plasticizing agents for PVC by Waldo Semon of the BF Goodrich Company in the late 1920s and early 1930s permitted BF Goodrich to introduce PVC-coated fabrics into U.S. markets in 1931. The PVC/plasticizer blends were used to make products such as raincoats and umbrellas with a solvent-based casting process. About the same time, IG Farben was reported to have begun manufacturing similar products in Germany.[2] The subsequent development of suitable heat-stabilizing additives was the final technological development that enabled PVC to expand into other applications and become a commercially viable plastic. Flexible PVC became very important as a rubber substitute during the rubber shortages encountered during World War II. After World War II, the unique properties of flexible PVC enabled it to quickly find a plethora of other uses.

Dramatic advances in rigid PVC processing technology were made during the late 1940s and throughout the 1950s. This, coupled with similar advances in stabilizer, lubricant, process aid, and impact modifier additive technology, helped to facilitate the processing of rigid PVC compounds. Soon thereafter, rigid PVC gained a firm and rapidly growing foothold in markets previously dominated by materials such as wood, steel, and iron. At this time, major differences emerged between U.S. and European rigid PVC compound and process technologies. In the years following World War II, Europeans faced raw material shortages as their devastated chemical industry was being rebuilt. This led to an emphasis on tackling rigid PVC manufacturing issues through process and equipment technology. Since the U.S. chemical industry escaped the war relatively unscathed, U.S. development efforts tended to emphasize additive and formulation technology.[3] To this day, significant differences still exist between U.S. and European rigid PVC processing and formulation practice.

The other major chapter in the history of PVC involves the linking of VCM exposure to a rare form of liver cancer called angiosarcoma. In 1974, BF Goodrich announced that four of its workers had contracted angiosarcoma. All those afflicted were directly involved with the PVC resin manufacturing process. Shortly thereafter, abnormally high numbers of angiosarcoma cases were confirmed among employees of other PVC resin manufacturers throughout the world. Workers involved in the charging and cleaning of PVC reactors were especially prone to this type of cancer. VCM was identified as the culprit and PVC manufacturers rapidly implemented new manufacturing processes to greatly reduce worker exposure to VCM. PVC resin manufacturers also added a VCM stripping step in the manufacturing process, which virtually eliminated residual VCM in the PVC resin. The total number of angiosarcoma deaths attributed to VCM exposure worldwide is believed to number less than 150.[4] Since these manufacturing changes were implemented, no angiosarcoma cases have been linked to the manufacture of PVC resin. It is also important to note that no angiosarcoma cases have ever been conclusively linked to workers manufacturing products containing PVC resin.[5]

Total PVC resin production in the United States during 2003 was approximately 14.7 billion pounds.[6] About 14 billion pounds of this PVC resin production was homopolymer resin manufactured by either the suspension or mass polymerization