The Technology of Plasticizers

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SERIES PREFACE

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PREFACE

We have tried to write the kind of book that we wish had existed when we began work in this area many years ago. Someone suggested we select authors for different chapters and then edit the whole book. Yet we envisioned a continuity and unity that we felt could not be achieved that way. There are, therefore, areas of complete ignorance which might not have been there had we chosen the editorial route. But as we look outward in all directions from the heart of plasticizers (which is where we live), we hope that the presentation of an overall perspective more than offsets these gaps in information.

We wished to cover all resins which might be plasticized, but settled for plasticizers for and plasticization of polyvinyl chloride (PVC) except in sections on theory and history. Since PVC takes the lion's share of commercial plasticizers this did not seem such a drastic cut. Also, there were good books on plasticization of many of the older resins and rubbers but none which gave comparable coverage of plasticization of PVC; and there were none which we felt adequately brought together and explained the various theories which apply.

As an immediate consequence we have written for the young researcher in polymer and plasticizer application areas. This implies that we have also written for the fabricator who needs to know how plasticizers affect processing of his resin, and which one will most closely give the final properties he wants. We also had in mind a formulator whose customers complain that her product did not do its job right or did not last as long as it should have and who does not know why. We have written for the plasticizer salesman who must answer his customers' questions. We have not forgotten the polymer scientist who feels that anything added to his polymer must surely adulterate it. The university professor and the good student who want to broaden their understanding of nature and of matter around and within us should find much that is helpful. Of course we have written it for ourselves and for others still maturing in these fields, so we have pointed out objectives that should be attainable. If perchance any comment seems to wander, any reference seems divergent, it may be included in the hope that we may reach some of the long-range goals before the next person, but if not, that someone at least may reach them.

We are indebted to a host of people without whom this book would not exist. Some of the help was highly technical, but some had to be human and personal. Arthur K. Doolittle, as our consultant, made the first audible suggestion that we ought to write the book. He guided in much of the early thinking, and at a moment when it looked impossible, Art encouraged with the comment, "Every job I ever tackled was over my head." John B. DeCoste, as consultant, studied the manuscript, eliminated several errors, and guided us to many valuable literature references. We have taken hundreds of Jack's suggestions, but a few times we did not. Consequently if there are errors they are not his but ours.

Within Monsanto we owe special thanks to Martin W. Farrar, Director, Research and Development, Plasticizers Division, and to Norman W. Touchette, Manager, Plasticizer Application Research and Marketing Technical Service, for their patience as this work progressed, for constructive criticism, and through them for permission from Monsanto for us to publish. Without the work and cooperation of the men and women, past and present, of our Plasticizer Synthesis and Application Laboratories this work could not have been done. Many of these people are named in references in various chapters. If the book covered all we originally desired, many other names of equal importance would have appeared. We are also indebted to the many technical men and women among our customers who through the years have taught and guided us in the uses and needs for plasticizers.

A special kind of appreciation goes to Ruth Zacher for the thousands of things that had to be done: typing, retyping, correcting reference styles and misspelled words. And we thank those who helped her at crash moments—Virginia Wolf, Georgia Schilling, Lisa Stann, and JoAnne Crutcher. Larry Beckett drew hundreds of figures which we had adapted to tell the plasticizer story the best way we knew how. Paula Raizman and others translated scores of articles from many languages for us.

Personally I owe a debt to my co-author J. R. Darby, known to readers on five continents as Joe, who paved the way with his struggle to get the industry committed to plasticization of PVC at a time when PVC was a questionable entity. He taught those of us who worked under him an especial awareness of the customer's problem and a detectivelike interest in solving it.

A book is always backed by significant small events. There was the cooperation of my wife, Sarah, as she drove while I indexed reprints. Again and again, she and our children helped set up office in a vacant farmhouse on the old home place in Kentucky, so I could write while the children played, until they felt we could do nothing normal until the book was finished. There are two others who unknowingly shaped the book and determined what the reader must contend with. My father as a professor of English—Shakespeare, Chaucer, and the like—instilled in me a love for literary research, but it was my mother who turned me to chemistry as a child, when she told how you can make water by burning hydrogen. The concept and its implications fascinated me, and I never got over it.

J. Kern Sears

Webster Groves, Missouri
August 1981

CONTENTS

CHAPTER 1

Plasticizers: What and Why

Almost every available polymeric material has been or can be used as a material for surface coatings, film, sheeting, small articles, or even for massive engineering structures. Yet the preparation of useful articles from any polymeric material is virtually impossible without auxiliary materials or additives. For coatings these may be solvents, thinners, stabilizers, oxidation inhibitors, oxidation promoters, defoamers, leveling agents, fungicides, pigments, and plasticizers. In a rubber they may be vulcanizing agents of many kinds, antioxidants, antiozonants, reinforcing fillers, nonreinforcing fillers, extender oils, and plasticizers. In a thick article they may be stabilizers, UV absorbers, pigments and dyes, reinforcing fibers, particulate fillers, lubricants, flow aids, impact modifiers, odor masks, special fragrances, and plasticizers. Rare is the case when a simple polymer is used alone. Occasionally a polymer such as polymethyl methacrylate may be used without modifiers, but some of the formulations for plastic articles leave the distinct impression that the resin is the matrix used to hold the additives together.

We are concerned with plasticizers and plasticization. This includes the behavior of the plasticizer with the base polymer or resin and its potential interactions with other additives. When some other additive, such as a pigment or dye, acts like a plasticizer, that is a part of our concern. We attempt to explain why plasticizers act as they do and to give examples of their performance as related to processing behavior and end-use properties.

A. DEFINITION

A plasticizer is a material incorporated in a plastic to increase its workability and its flexibility or distensibility (elongation). Addition of the plasticizer may lower the melt viscosity, the temperature of the second-order transition, or the elastic modulus of the plastic (2). Sometimes the plasticizer may not be added as a separate material but may be produced *in situ* by cleaving occasional polymeric molecules to produce smaller ones. According to theory, plasticization on the molecular level is the weakening or rupturing of selective bonds, between molecules, while leaving others strong, to make possible the shaping, flexing, or molding of the material. Accompanying this, there is increased intermolecular space (free volume), which makes room for the change in shape. These processes profoundly affect us and the world we live in. They may be seen in improved softness, "drape," or "hand" in plastic sheeting, greater toughness and impact strength in a molded article, better flow-out in powder coatings, or edge covering in fluid bed processes, and leveling in various paints. Plasticization may result in good flexibility in automobile seat covers in winter, or in car tires in arctic weather, or in good adhesion of a paint on a flexed, cold metal substrate.

Of great practical importance, the plasticizer permits a processor to start with one basic resin and develop different products, many times proprietary ones, with a wide range of properties for different applications.

One example analogous to the present art is the use of the plasticizer, water, and the tough horny resin, gelatin. The final product is prepared by heating until the gelatin dissolves into the water, and then cooling until it gels into a soft, flexible "solid," which is palatable when other additives are present to give it the right color, flavor, and aroma. By change in formulation the product may be a congealed salad, a gelatin dessert, a marshmallow, or rope licorice candy. Gelatin had a brief industrial life as a surface coating material when it was used as a temporary coating for plate glass. As it dried, the polymer film shrank and adhered so tenaciously to the glass that chips of glass were pulled from the surface to create translucent panes for windows and doors. This high degree of adhesion is usually desired but not always achieved in surface coatings. The unique gelatin process capitalized on what would normally be a plasticizer fault—volatility. Volatility was a serious fault in colored gelatin or "patent isinglass" films used in front of the footlights and borders in most theaters until shortly before World War II. While giving light of just the right hue of red, blue, and amber for each dramatic scene in a play, the films would shrink, split, and fail from loss of plasticizer—water and glycerine. Plasticizers with lower volatility were badly needed. The one alternate film, Celluloid, was unacceptable because of its near-explosive flammability.

The preparation of gelatin products oversimplifies plasticization and tends to narrow our vision of how broad the definition really is. Yet it still holds true that the resin and the plasticizer must be intimately mixed, and that for most plasticized products this is commonly done by heating until the resin has dissolved into the plasticizer or the plasticizer has dissolved into the resin. The material is then formed, or coated onto a substrate, and cooled. Alternatively, the resin and plasticizer may be mixed by dissolution in a common solvent without heat. Evaporation of the solvent, as is common in lacquers, paints, and inks, leaves the plasticized resin. Plasticizer effects are dramatically shown in several ways when a high molecular weight polyvinyl chloride (PVC)* homopolymer is fluxed on a hot roll mill. At 160°C the resin particles pour, unchanged, like sand between the rolls. If the temperature is raised, the resin softens and eventually forms a tough sheet around one of the rolls. While it is softening and sheeting out on the mill, it is also decomposing from excessive heat. The final sheet, when cooled, is brown to black, horny to brittle, corrosive from liberated hydrogen chloride, and worthless. If, on the other hand, a combination of a plasticizer such as di-2-ethylhexyl phthalate (DOP) and resin is placed on the roll mill at 160°C, the resin softens and fuses; the mass quickly becomes homogeneous and forms a sheet around one roll. When the sheet is removed and cooled, it is clear, colorless to faintly yellow, noncorrosive, and semirigid to very flexible, depending on the amount of plasticizer used. This is a simplified version of the more sophisticated formulations entering the multimillion dollar market of plasticized polymers.

Many high molecular weight materials, organic and inorganic, are benefited by plasticizers, yet our major emphasis is on organic plasticizers for synthetic organic polymers and particularly for PVC.

Organic plasticizers are usually moderately high molecular weight liquids or occasionally low-melting solids. Most commonly, they are esters of carboxylic acids or phosphoric acid. Other types used include hydrocarbons, halogenated hydrocarbons, ethers, polyglycols, and sulfonamides. We occasionally touch on others.

B. RELATIONSHIPS AMONG MODIFIERS

The concept of "plasticizer" as it is defined above is broad. There is a constant tug-of-war that tends to narrow it as new terms are invented, or to broaden it as new areas of performance are discovered.

Figure 1.1 shows a map of several types of polymer modifiers. There is no distinct dividing line between their territories. Each area is a part of a complex "lapland." At the extreme lower right are the typical solvents. These are always rather low in molecular weight and must have a high degree of compatibility with

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* Throughout the book PVC will stand for polyvinyl chloride rather than pigment volume concentration as is usual in coatings literature.

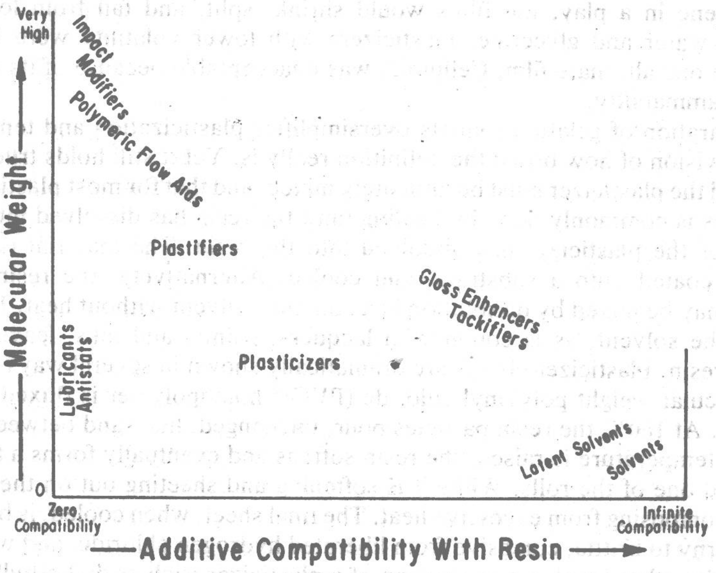

Figure 1.1 Polymer modifier map showing roughly what effects may be achieved in modifying a resin by additives that differ in molecular weight and that vary in compatibility or thermodynamic solubility.

the resin to be considered solvents at all. At this point we are equating *compatibility* with thermodynamic solubility, a concept that will be broadened in Chapter 3. *Latent solvents* or *theta solvents*, which must be heated above room temperature to show their solvent power or which must be blended with a good solvent to be useful, lie to the left of the location for true solvents on the map. We may begin at this point—latent solvents—to explore the map by considering specific compounds and the hypothetical transmutations that would be necessary to convert one compound into another and consequently one type of additive into another. The resin foremost in our mind for modification will be PVC, but other resins and rubbers will be included.

Ethyl acetate is an excellent solvent for many polymers, but for PVC it is only a latent solvent. If we could dimerize it at the acetic alpha carbon, we would produce diethyl succinate, which would be an even poorer solvent and would take on the properties of a plasticizer (see the Appendix for structural formulas of typical plasticizers). It would lie slightly above and to the left of the latent solvent region. Increasing the size of the carbon chains by a total of 14 carbons could result in dioctyl adipate (DOA), a plasticizer with good compatibility in PVC and a moderate to high degree of lubricity. DOA would lie slightly to the left of center on the map. Elimination of one of its ester groups and a slight shift of carbon atoms could produce butyl stearate, which has very poor compatibility in PVC but can be used as a plasticizer in small amounts with other more compatible plasticizers. It is very lubricating. Hydrolysis would convert it to stearic acid, the most commonly used lubricant in plastic processing. The imbalance of the extreme hydrogen bonding ability and polarity at one end of the stearic acid molecule, and its extreme nonpolar nature at the other results in almost total incompatibility in PVC. Yet the small amount of stearic acid that is compatible is a very efficient plasticizer. Returning momentarily to ethyl acetate at the latent solvent position on the map, we may hypothetically cyclize it and remove its carbonyl oxygen to obtain tetrahydrofuran (THF), one of the best solvents known for PVC. Thus we have spanned the breadth of the lower regions of the map.

We may similarly explore other regions of Figure 1.1. In the plasticizer region we begin with DOA. If the adipate structure were in some way cyclized and aromatized (with addition of two carbons) dioctyl phthalate (DOP) would result. DOP, for 30 years the most popular plasticizer for PVC, would lie at about the midpoint of the map from left to right, noticeably to the right of DOA. As a plasticizer it is completely compatible with PVC, but as a solvent it is very poor. It will dissolve only about 2% PVC at room temperature without gelling. If DOP were in some way cyclized still further and perhaps dimerized into products similar to rosin and rosin dimer derivatives, with increased density and refractive index, these would act as tackifiers in rubber processing and as gloss enhancers in surface coatings.

We are not restricted to carboxylic acid ester functionality in contemplating these transmutations. In the world of reality, *N*-ethyl *o,p*-toluene sulfonamide (mixed *o*- and *p*-isomers) is a plasticizer lying somewhere between latent solvents and general purpose plasticizers like DOP. Its closely related, low molecular weight polymer made from toluene sulfonamide and formaldehyde has long added gloss and good adhesion to a wide variety of lacquers including fingernail polish.

Among the more important plasticizers are phosphates such as 2-ethylhexyl diphenyl phosphate. Its moderately high dielectric constant permits the gradual dissipation of a static charge from plastics containing it. If, however, one of its phenyl groups were removed by hydrolysis, the partial ester would have low compatibility with PVC; its increased hydrogen bonding ability and hydrophilic nature would make it a much more powerful antistat.

If the molecular weight of a given plasticizer-type molecule is increased (maintaining the same percentage of functional groups), its position on the map moves upward toward the left as its increase in molecular weight automatically makes compatibility with PVC or other resins more difficult. Thus chlorinated paraffin hydrocarbon plasticizers with a molecular weight of about 500 or polyester plasticizers with molecular weights of about 1000 to 3000 would occupy the upper position of the plasticizer region and particularly that toward the left, toward the *plastifier* region. If the molecular weight is increased further but the structure and functional groups are adjusted to give adequate compatibility and yet maintain a reasonably linear configuration, a liquid or rubbery polymeric additive called a plastifier, may be produced. Among these are high molecular weight polyesters, ethylene vinyl acetate (EVA), nitrile rubbers (SAN), and chlorinated polyethylenes (CPE). These can be used in place of part or all of the conventional plasticizer in some compositions to give flexibility and processability. Yet in some of their properties they are typically polymeric and are therefore considered *resin extenders* at times.

If the plasticizerlike molecule is maintained essentially linear but perhaps with short branching, and it is increased a high molecular weight (e.g., a million), even higher than the base polymer in which it is used, yet with noticeable compatibility in the polymer, it can become a *polymeric flow-aid*. Certain polymeric esters have this ability. They may eliminate melt fracture during processing. By modifying flow behavior they help eliminate surface defects—ripples, pits, craters, ''orange peel,'' and the like. At times it seems as if they are lubricants or perhaps surfactants or more conventional plasticizers, but always somehow they are different because of their very high molecular weight. If the molecular weight goes even higher (as by cross-linking), and compatibility lower, the rubbery product becomes a very efficient plasticizer but is so localized by incompatibility that it must be carefully distributed throughout the resin to exert its influence as an *impact modifier* or *particulate plasticizer*.

In all of this, the concept of ''plasticizer'' is central. Since there are no hard and fast boundaries surrounding it, we will illustrate and attempt to explain what happens when we stray from the more conventional plasticizer types toward the fringes of compatibility and molecular weight. We find plasticizers that lubricate and those that improve gloss. We find plasticizers acting as true solvents, or as antistats, and we find impact modifiers that are plasticizers.

We have not included on the map many other additives such as stabilizers and antioxidants, which though used in small amounts, frequently act as lubricants or plasticizers, nor have we included pigments, fillers, and the like, which have approximately zero solubility. When these produce effects similar to those of a plasticizer they may be briefly considered, as well as when they interact in some way with the plasticizer.

C. POLYMERS BENEFITING FROM PLASTICIZERS

Our major emphasis is on plasticization of polyvinyl chloride (PVC) since its technology accounts for 75% or more of the commercial materials usually considered plasticizers. Yet for perspective, we should scan the field to appreciate how plasticizers of many kinds modify the properties of almost every polymer, organic and inorganic, around us or within us. The most ubiquitous plasticizer is water (unless it is air), which prevades our world. Protein in living organisms is supple because its water content controls the hydrogen bonding that otherwise would give it the tough consistency of beef jerky. Under conditions of high temperature and pressure inside the earth, water disrupts cross-linking bonds in numerous minerals and plasticizes the rocks, enabling them to flow (46,78). So the shifting earth crust and earthquakes appear in part as a result of plasticization. When Dorothy Parker wrote, ''The willow was winding the moon in her tresses (72),'' she was not speaking of dry, unplasticized cellulose and lignin. Other natural plasticizers, such as fats and oils, help give pleasant texture to foods, pliability to leather, and play a role in the human aging processes.

Commerical polymers are very commonly modified by plasticizers. Aside from PVC, the semisynthetic cellulose esters and ethers consume moderate amounts of plasticizers in order to be formed at all. Plasticizers give them resistance to mechanical shock when they are used for screwdriver handles. Nylons frequently require small amounts to aid processing and avoid thermal decomposition. At times, small amount of plasticizers keep the final nylon article from being too brittle for its intended job. Plasticizers called *dye carriers* swell and soften fibers of polyesters, nylons, and acrylonitile copolymers to permit dye pick-up. Plasticizers, in small amounts, aid in processing thermosets, such as phenolics and melamines, and are used to give good "cold punch" properties and avoid shattering during cutting operations. Even the completely amorphous resins, such as most of the acrylics and polystyrene, which as thick compositions may require no plasticizer, make use of plasticizers when they are used in paints. One plasticizer aids in film formation from latex paints, and a second helps avoid the unsightly appearance at the lap when you have painted your way around the room and reach the semidry paint at the starting point. Delayed tack and hot-melt adhesives made of polystyrene, cellulosics, or polyethylene with plasticizers, which are solid at room temperature, are growing industrially even though they make use of one of the earliest concepts in modern plasticizer technology, the one that set the Hyatt brothers on the proper trail to Celluloid. Rubbers included large amounts of *extender oils* (which are *secondary plasticizers*) in automobile tires and at times use the more typical ester plasticizers to get the final elongation and low temperature properties needed. For self-adhesion, so necessary in rubber compounding, and for tackiness of pressure-sensitive adhesives, tackifying plasticizers are used.

D. EXTERNAL VERSUS INTERNAL PLASTICIZATION

The plasticizer as we most commonly consider it is a discrete material that is added to the polymer, but for the most part never chemically combined with it. This is *external plasticization*. There are times when the original polymer can be modified chemically, or a related polymer can be synthesized that will have more flexibility or better low temperature properties. Development of the desired properties in the polymer itself is called *internal plasticization*. External plasticization permits the greatest latitude in formulation and properties and is generally far less expensive. However, when a specific large-scale use is developed for a plasticized resin, commercial interests frequently demand that an internally plasticized resin be tailored to that end-use. The final product is usually an internally plasticized resin that comes close to the desired properties, but which still requires an external plasticizer in small amounts to achieve the best performance (58).

E. HISTORICAL PERSPECTIVE

1. Primitive Technologies

Man has always been astoundingly creative, and his use of plasticization techniques accompanies the earliest records. Our technology today is a hybrid of art and science, having its roots in the successes of forgotten inventors. Water is the processing plasticizer used for clay to make pottery or the clay tablets of the Tigris-Euphrates River valley, in which the earliest history of plasticization was pressed; this seems so natural we forget its significance. Water was used by the artists in the caves of Altimara, Spain, for their calciminelike paints (42). Surface coatings from that time on form the most direct evolutionary line for today's plasticizer industry. The occasional preparation of thick articles from surface coating materials helped bridge the gap when the modern plasticizer industry began.

Simple plasticization procedures have always been common even on massive objects. When the American Indian soaked rawhide in water to swell it, shape it, and tool it before hardening and cross-linking the collagen with the aldehydes in the smoke of his fire, he was using water as a temporary plasticizer in the manufacture of thick, expanded shields. Neat's-foot and sperm oil applied to leather are more permanent plasticizers. There is an obvious relationship between Eskimos' chewing seal skins to soften them for clothes, and the mechanical mastication of rubber and other very high molecular weight polymers, which lowers the molecular weight and creates plasticizing fragments and end-groups. No historical connection exists. Rather, there are multiple inventors.

Pioneer women soaked straw in water for manufacture of brooms and hats. Farmers waited for rain to soak their oak lumber so they could drive nails through it to build barns. Bent-wood chairs and huge ship timbers were shaped to the 'loft drawings' by soaking or steaming—the inventors are long forgotten. Tung oil, a polymerizable plasticizer normally used in paints and varnishes, was converted to the ancient Chinese lacquer vases, layer by layer, dried and carved. Casein, a natural molding resin, was adapted to surface coating by the Shakers as they mixed buttermilk and brick dust to decorate simple furniture with the highly durable "Shaker Red." The paint was flexibilized just enough by salts of lactic acid, a modern leather plasticizer.

Plasticization is thus so natural to us that the development of basic processes and equipment was lost. But 4,000 years ago, the *Ark*, a ship half the length of the *Queen Mary*, was waterproofed and caulked with pitch (44). The Gilgamish account shows the pitch was plasticized with "oil." Similar asphalt or bitumen compositions were used as protective coatings for punt poles. Artists' paints are also mentioned but no technology given (34).

Other complex polymeric substances (horn, tortoise shell) and simpler natural resins, gums, and waxes were brought into widespread commerce (5, 42, 59) and found their way into articles through plasticization processes. By the time chemistry had advanced far enough to make the first semisynthetic resin, cellulose nitrate, industrial techniques were well advanced. These techniques included milling and compression molding, calendering, laminating, cloth coating, beating (cellulose fibers for paper), latex casting, and so on (21, 22, 23, 95). Rosin, shellac, and gutta-percha were the resins which inspired some of the finest of the plastic techniques. One polymer alone had the properties of resilience, toughness, and elongation extraordinary enough to fire the imagination of the European world when reports of it and then samples were brought back by Spanish explorers from the Americas. Called *caoutchouc* by the Indians of South America (*cao*, wood; *o-chu*, to weep) natural rubber came as a latex from "weeping" slits through the bark of *Hevea Guyanensis* trees. It set a goal for resin and plasticizer chemists to work toward. The technologists of the New World had already used it to waterproof cloth. They had shaped it into boots and of course into the inevitable ball " 'Very well. Let us play ball, boys,' said the Lords of Xibalba" (81).