

PLASTICIZERS

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Introduction

A plasticizer is a material that when added to another substance, makes that material softer or more flexible. Although this definition can include many products, from water added to clay for production of pottery to lime mixed with concrete to make it more workable, the word "**plasticizer**" generally refers to materials used in plastics. The Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of a plasticizer: A plasticizer is a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility. In addition, a plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product.

Early plasticizer technology and development focused on nitrocellulose. One of the first commercially important plasticized products was Celluloid, which was cellulose nitrate plasticized with camphor. John Wesley Hyatt patented this technology in 1870 (1). Later developments included the use of triphenyl phosphate as a low flammability plasticizer for cellulose nitrate. In the 1920's, the increasing demand for plasticized nitrocellulose paints lead to the development of two more important plasticizers, tricresyl phosphate and dibutyl phthalate.

Although polyvinyl chloride (PVC) was first produced in the middle of the nineteenth century, it was Waldo Semon's vision of the usefulness of plasticized PVC that initiated the growth of the flexible PVC industry. In 1933, Semon patented the use of solvents such as o-nitrodiphenyl ether, dibutyl phthalate, and tricresyl phosphate to

produce a "rubber-like composition" with many different uses (2). Soon afterwards, the use of di-2-ethylhexyl phthalate or DOP (patented by Monsanto in 1929 for plasticization of nitrocellulose (3)) was applied to PVC. In the period that followed, thousands of products were tested and evaluated as plasticizers. DOP became commercially available in the 1940's and since then has remained one of the most important plasticizers for polyvinyl chloride.

There are presently about 450 different plasticizers produced worldwide, although only about 50 of these are classified as commercially important. Approximately 90% of these products are used in the production of plasticized or flexible polyvinyl chloride (PVC) products. Other polymer systems that use small amounts of plasticizers include polyvinyl butyral, acrylic polymers, poly(vinylidene chloride), nylon, polyolefins, and certain fluoroplastics. Plasticizers can be used with rubber, although more often these materials fall under the definition of extenders, rather than plasticizers. The 1998 estimated worldwide production of plasticizers approached 9 billion pounds. Over 85% of this volume were phthalic acid esters. A listing of the major plasticizers and their compatibilities with different polymer systems is shown in Table 1.

Mechanism of Plasticization

For a plasticizer to be effective, it must be thoroughly mixed and incorporated into the polymer matrix. With organic polymers, this is typically performed by heating and mixing until either the resin dissolves in the plasticizer or the plasticizer dissolves in the resin. The material is then formed into the useful product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting physical properties of the flexible product.

Several theories have been developed to account for the observed characteristics of the plasticization process; Sears and Darby (4) have prepared a significant review of the theoretical treatment of plasticization. Although most mechanistic studies have focused on PVC, much of this information can be adapted to other polymer systems. According to **the lubricating theory of plasticization**, as the system is heated, the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions. **The plasticizer molecules act as shields to reduce polymer-polymer interactive forces and prevent the formation of the rigid network.** This reduction in intermolecular or van der Waals forces along the polymer chains increases the flexibility, softness, and elongation of the polymer.

The gel theory considers the plasticized polymer to be neither solid nor liquid but an intermediate state loosely held together by a three-dimensional network of weak secondary bonding forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecule or polymer chain movement. This has the effect of making the polymer system more

Table 1 - Plasticizers and Plasticizer Compatibility ^a

Plasticizers	Compatibility with plastics ^b								
	CA	CAB	CN	EC	PM	PS	VA	VB	VC
Adipic acid derivatives									
di-n-hexyl adipate (DHA)	P	C	C		C		P	C	C
heptyl nonyl adipate (79A)	I	C	C		C		P	C	C
di-2-ethylhexyl adipate (DOA)	P	C	C	C	P	C	I	P	C
diisodecyl adipate (DIDA)	P	C	C	C	P	C	P	P	C
diisononyl adipate (DINA)	P	C	C	C	P	P	P	P	C
Azelaic acid derivative									
Di-2-ethylhexyl azelate (DOZ)	C	C	C	C			P	I	C
Benzoic acid derivatives									
diethylene glycol dibenzoate	P	C	C	C	C	C	C	C	C
dipropylene glycol dibenzoate	P	C	C	C	C	C	C	C	C
2,2,4-trimethyl-1,3-pentaneodiol-isobutyrate benzoate	I	C	C	P		C	C		C
Citric acid derivatives									
tri-n-butyl citrate	C	C	C	C		C	C	C	C
tri-n-butyl acetylcitrate	P	P	C	C		C	C	C	C
Epoxy derivatives									
epoxidized soybean oil (ESO)	I	P	C	C	I	I	I	I	C
epoxidized linseed oil (ELO)	P	C	C	P	P	I	I	I	C
2-ethylhexyl epoxy tallate	I	C	C	C	I	I	I	C	C
Glycol derivatives									
diethylene glycol dipelargonate	I	C	C	C			P	C	C
triethylene glycol di-2-ethylbutyrate	I	P	C	C	C		C	C	C
Hydrocarbons									
hydrogenated terphenyls	I	C	C	C		C	C	C	C
chlorinated paraffin (52 wt% Cl)						C	C		C
Isophthalic acid derivatives									
di-2-ethylhexyl isophthalate	I	C	C	C	P	C	I	C	C
Oleic acid derivatives									
butyl oleate	I	C	C	C		C	C	C	P
Phosphoric acid derivatives									
tri-2-ethylhexyl phosphate (TOF)	P	P	C	C	I		I	C	C
triphenyl phosphate (TPP)	C	C	C	C	C	C	C	C	P
tricresyl phosphate (TCP)	C	C	C	C	P	C	C	C	C
2-ethylhexyl diphenyl phosphate	P	C	C	C	C	C	C	C	C
isodecyl diphenyl phosphate	P	C	C	C	C	C	C	C	C
Phthalic acid derivatives									
dimethyl phthalate (DMP)	C	C	C	C	C	C	C	C	C
diethyl phthalate (DEP)	C	C	C	C	C	C	C	C	C
dibutyl phthalate (DBP)	C	C	C	C	C	C	C	C	C
butyl octyl phthalate (BOP)	I	C	C	C	P	C	P	C	C
diisohexyl phthalate (DHP)	P	C	C	C	C	C		C	C
diisoheptyl phthalate (DIHP)	I	C	C					C	C
heptyl nonyl phthalate (79P)	I	C	C	C		C	I	C	C
heptyl nonyl undecyl phthalate (711P)	I	C	C	C	C	C	I	P	C
diisooctyl phthalate (DIOP)	I	C	C	C	C	C	C	P	C
di-2-ethylhexyl phthalate (DOP)	I	C	C	C	C	C	I	P	C

Table 1 (Continued), Plasticizers and Plasticizer Compatibility ^a

Plasticizers	Compatibility with plastics ^b									
	CA	CAB	CN	EC	PM	PS	VA	VB	VC	
Phthalic acid derivatives, continued										
(n-hexyl, octyl, decyl) phthalate (610)	P	C	C	C	P	C	P	C	C	
(n-octyl, decyl) phthalate (810P)										
diisodecyl phthalate (DIDP)	P	C	C	C	C	C	C	C	C	
diundecyl phthalate (DUP)										
ditridecyl phthalate (DTDP)	P	C	C	C	P	C	P	C	C	
butyl benzyl phthalate (BBP)	P	C	C	C	C	C	C	C	C	
alkyl benzyl phthalate, Santicizer ® 261	I	C	C	C	C	C	C	C	C	
Polyesters										
adipic acid polyester (mol wt 6000), Paraplex ® G-40	I	C	C	P			C	I	C	
adipic acid polyester (mol wt 2000), Santicizer ® 334F	I	C	C	P	I	C	C	P	C	
azelaic acid polyester (mol wt 2200), Platolein ® 9720	P	C	C	I	I	I	P	P	C	
sebacic acid polyester (mol wt 8000), Paraplex ® G-25	I	I	C	I			P	P	C	
Ricinoleic acid derivatives										
methyl ricinoleate	P	C	C	C	P		C	C	I	
n-butyl acetylricinoleate	I	C	C	C	P	P	C	C	C	
castor oil		P	P	C	P			C	C	
Sebacic acid derivatives										
di-2-ethylhexyl sebacate (DOS)	I	P	C	C	C	C	P	P	C	
Stearic acid derivatives										
n-butyl stearate	I	C	P	C	I	P	I	I	P	
Sucrose derivatives										
sucrose acetate-isobutyrate (SAIB)	C	C	C	C	C	C	C	P	I	
Sulfonic acid derivatives										
(o,p)-toluenesulfonamide	C	C	C	C	C	P	C	C	P	
N-ethyl-(o,p)-toluenesulfonamide	C	C	C	C	C	C	C	C	P	
alkylsulfonic acid ester of phenol and creosol, (Mesamoll ®)	I	C	C	C	I	C	I		C	
Terephthalic acid derivatives										
bis(2-ethylhexyl)terephthalate (DOTP)	I	C	C		C	C		C	C	
Trimellitic acid derivatives										
tris(2-ethylhexyl) trimellitate (TOTM)	C	C	C	C	C	P	P	P	C	
heptyl nonyl trimellitate (79TM)	I	C	C	C	C	C	I	C	C	
triisononyl trimellitate (TINTM)							I		C	
Terpenes and derivatives										
camphor	C	C	C		C				C	
hydrogenated methyl ester of rosin	I	C	C	C		C	C	C	C	

^a data from Sears and Touchette (5)

^b Resins used: CA, cellulose acetate; CAB, cellulose acetate-butyrate; CN, cellulose nitrate; EC, ethylcellulose; PM, polymethyl methacrylate; PS, polystyrene; VA, polyvinyl acetate; VB, polyvinyl butyral; VC, polyvinyl chloride. Code for compatibility: C, compatible; P, partially compatible; and I, incompatible.

flexible. Free volume can be increased through modifying the polymer backbone, such as by adding more side chains or end groups or by adding small molecules with flexible end groups. The free volume theory builds on both the lubricity and gel theories of plasticization.

The mechanistic explanation of plasticization looks at the interactions of the plasticizer with the resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the resin molecule but are free to self-associate and to associate with the polymer molecule at certain sites. As these interactions are weak, there is a dynamic exchange process whereby as one plasticizer molecule becomes attached at a site or center it is rapidly dislodged and replaced by another. Different plasticizers will yield different plasticization effects because of the differences in the strengths of the plasticizer-polymer and plasticizer-plasticizer interactions. At low plasticizer levels, the plasticizer-PVC interactions are the dominant interactions while at high plasticizer concentration ranges, plasticizer-plasticizer interactions can become more important.

For a plasticizer to be effective and useful in PVC, it must contain two types of structural components. The polar part of the molecule must be able to bind reversibly with the polymer while the non-polar portion of the molecule adds free volume and contributes shielding effects at other polar sites on the polymer chain. The balance between the polar and non-polar portions of the molecule is critical; if a plasticizer is either too polar or too non-polar, compatibility problems can arise. Useful tools in estimating plasticizer compatibility are the A_p/P_o Ratio method developed by Van Veersen and Merelaenbergh (6) and the solubility parameter methods (7,8).

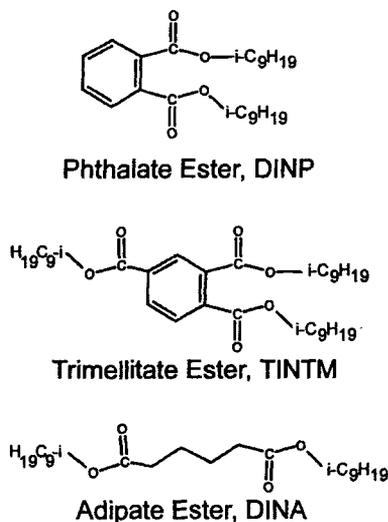
Types of Plasticizers

Flexible polymeric systems can be obtained through internal and external plasticization techniques. Internally plasticized PVC is produced by the copolymerization of vinyl chloride with another monomer to obtain a more flexible polymer backbone or by grafting another polymer onto the PVC backbone. External plasticization is achieved by incorporating a plasticizer into the PVC matrix through mixing and heat. These external plasticizers are classified as either monomeric or polymeric plasticizers depending upon their molecular weight. Plasticizers can also be characterized on the basis of their chemical structure. The three most important chemical classes of plasticizers are the phthalic acid esters, adipic acid esters, and trimellitic acid esters; these structures are shown in Figure 1. Di- and Tri-esters with a molecular weight range from 300 to 600 typically offer a balance of solvency and compatibility with the resin, yielding plasticized or flexible materials with useful properties and good aging abilities. Polymeric plasticizers are generally polyesters of molecular weights less than 6000.

Plasticizers can be divided into two classes based on their solvating power and compatibility with the polymer. **Primary** plasticizers are used as either the sole plasticizer or the major plasticizer component of the flexible polymer system. These materials can effectively solvate the polymer and will retain good compatibility upon aging. **Secondary** plasticizers are products typically blended with a primary plasticizer to improve certain performance attributes such as flame resistance, enhanced low

temperature flexibility, or to reduce formulation costs. Generally secondary plasticizers are not used as primary plasticizers because of high costs or performance disadvantages such as limited compatibility with the polymer system. The distinction between the primary and secondary plasticizer classifications can be arbitrary. It is possible that a plasticizer used in one formulation as a primary plasticizer could be used in a second formulation as a secondary plasticizer.

Figure 1. Primary Chemical Classes of Plasticizers



Most commercial plasticizers for PVC can be classified as belonging to one of three grouping (9); **general-purpose plasticizers**, **performance plasticizers**, and **specialty plasticizers**. General-purpose plasticizers are those products that offer optimum performance at the best economics and represent the largest class of plasticizers. This group includes diisononyl phthalate (DINP), di-2-ethylhexyl phthalate (DOP), and diisooheptyl phthalate (DIHP).

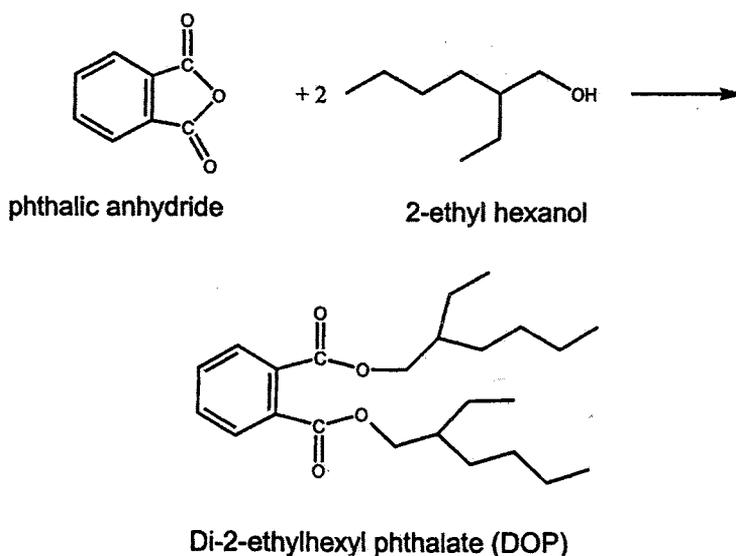
Performance plasticizers offer added performance benefits over general-purpose plasticizers, usually with additional formulation costs. This group of plasticizers can be subdivided into three groupings; fast solvating plasticizers, low temperature plasticizers, and low volatility plasticizers. Examples of performance plasticizers include the fast fusing plasticizers butyl benzyl phthalate (BBP) and dihexyl phthalate (DHP), the low temperature plasticizers di-2-ethylhexyl adipate (DOA) and di-n-undecyl phthalate (DUP), and the permanent plasticizers diisodecyl phthalate (DIDP), ditridecyl phthalate (DTDP), tri-2-ethylhexyl trimellitate (TOTM), and triisononyl trimellitate (TINTM).

The specialty plasticizer class includes several types of primary and secondary plasticizers. Generally these are used for unusually rigorous performance requirements

and provide important attributes such as increased stabilization, reduced migration, improved permanence, flame resistance, and reduced plastisol viscosity. Polymeric plasticizers, esters of citric acid, benzoic acid esters, brominated phthalates, and phosphate esters are a few examples of specialty plasticizers.

Phthalate Esters. Phthalate esters are prepared by the esterification of two moles of a monohydric alcohol with one mole of phthalic anhydride as shown in Figure 2. Although phthalate esters can be prepared from many different alcohols, the range of alcohols used to make plasticizers for PVC applications is generally limited from C4 to C13 alcohols. Phthalate esters prepared from alcohols below C4 are too high in volatility while phthalate esters prepared from alcohols greater than C13 have limited compatibility. Di-2-ethylhexyl phthalate (DOP), which is prepared from 2-ethyl hexanol, is still regarded as the industry standard. Diisononyl phthalate and diisodecyl phthalate have significant market presence in many parts of the world and are used in applications where improved performance over DOP is required. Together these three plasticizers account for over 80% of all PVC plasticizers usage.

Figure 2. Synthesis of Di-2-ethylhexyl Phthalate



Improvements in plasticizer performance can be obtained through choice of the alcohol used to make the phthalate esters. Krauskopf has examined (10) the alcohol structural relationships with plasticizer performance and has developed a number of correlations that can be used to predict plasticizer performance in flexible PVC as the molecular weight and the linearity of the alcohol is varied. The use of linear alcohols favors improved performance in reduced volatility, lower plastisol viscosities, and low temperature flexibility over branched alcohols of the same carbon number. The

phthalate esters prepared from C6 or C7 alcohols, for example dihexyl phthalate and diisooheptyl phthalate, fuse with PVC faster than the general-purpose plasticizers. The higher molecular weight C10 to C13 alcohols are used to prepare plasticizers for low volatility applications, such as those required for electrical cable insulation and sheathing.

Adipate Esters. Aliphatic dicarboxylic acid esters are prepared by the esterification of diacids such as adipic or azelaic acid with C6 to C10 monohydric alcohols. This class of plasticizer is used to extend the useful temperature range of plasticized PVC products, by providing increased flexibility at lower temperatures. Di-2-ethylhexyl adipate (DOA), which is prepared by the esterification of one mole of adipic acid with two moles of 2-ethyl hexanol, is the most important plasticizer in this class. Another important adipate is diisononyl adipate which offers greater permanence over DOA. Di-2-ethylhexyl azelate (DOZ), di-2-ethylhexyl sebacate (DOS), and diisodecyl adipate are used for extremely demanding low temperature applications or low temperature applications requiring lower plastisol volatility over that of DOA. The adipate and azelate esters may be used as primary or as secondary plasticizers.

Trimellitate Esters. Trimellitate esters are used as primary plasticizers in those applications where greater permanence is required. These esters are similar in structure to the phthalic acid esters, except for having a third ester functionality on the aromatic ring. Trimellitate esters offer advantages with greater permanence, either by reduced volatility losses or losses attributed to lower migration rates into other materials. Plasticized PVC electrical wire insulation prepared from either tri-2-ethylhexyl trimellitate (TOTM) or the more permanent plasticizer, triisononyl trimellitate (TINTM) will survive longer periods of high temperature service versus those products prepared from more volatile phthalate plasticizers.

Other Plasticizers. Polymeric plasticizers have found specialty uses due to their low volatility and high resistance to migration. These products are typically polyesters, with a molecular weight range from 1000 to 6000, and often prepared by the esterification of propylene glycol or butylene glycol with adipic acid. The higher viscosity of these products can cause processing problems in dry blending and in plastisol applications.

In order to improve the fire resistance characteristics of flexible PVC, phosphate esters can be used. PVC is inherently fire resistant compared to other polymer systems, but the presence of plasticizers reduces this property. Phosphate esters prepared from mixtures of either C8 or C10 alcohols with aromatic alcohols offer a compromise of flame reduction, volatility, and efficiency. Brominated plasticizers such as di-2-ethylhexyl tetrabromophthalic acid ester are also gaining importance as low-flammability plasticizers.

Although used only to a small extent in the US, the majority of the secondary plasticizers in use worldwide are chlorinated paraffins. Chlorinated paraffins are produced by chlorination of hydrocarbons and have a chlorine content in the range of 30 -70%. These secondary plasticizers are used to reduce cost and to improve fire resistance. Naphthenic and aliphatic mineral oils are also often used as secondary

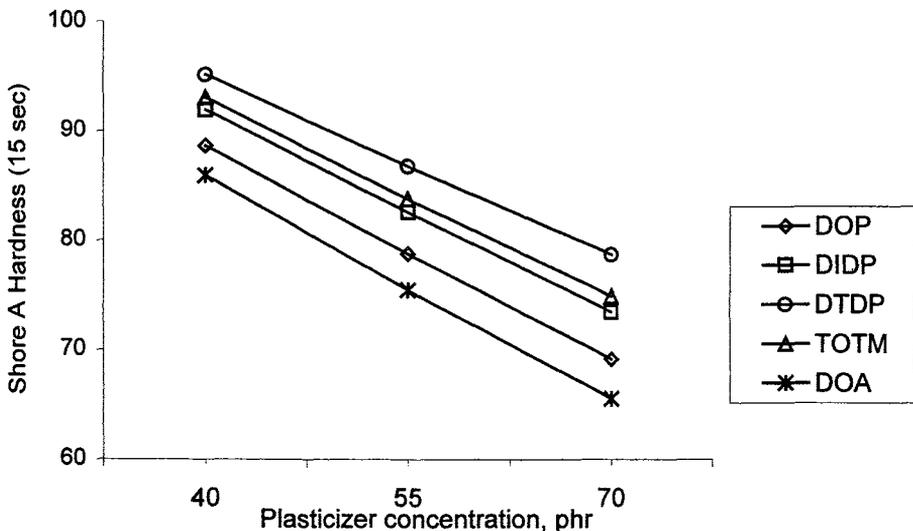
plasticizers to help reduce costs. Secondary plasticizers have limited compatibility with plasticized PVC and as the molecular weight of the primary plasticizer increases, compatibility problems increase.

Plasticizer Characteristics and Performance of Flexible PVC

A change in the type and level of plasticizer will affect the properties of the finished flexible article. The choice of plasticizer is almost always a compromise between performance requirements and product cost. Some of the more important properties that should be considered are listed in Table 2.

Plasticizer Efficiency. Plasticizers are added to materials to make them softer and more flexible; some plasticizers are more efficient at this than others. **Plasticizer efficiency** is used to describe the ability of a plasticizer to make the product softer and is reported as a ratio of the slope of the hardness versus plasticized concentration to the slope of that found for DOP. The relationship of hardness and plasticizer concentration expressed in phr (parts per hundred resin) is shown in Figure 3. Within a given series of esters having a common acid group, plasticizer efficiency increases as the molecular weight of the plasticizer decreases. Plasticizer efficiency improves as the linearity of the alcohol chain also increases.

Figure 3. Hardness versus Plasticizer Concentration



Plasticizer Solvency. To achieve a useful plasticized PVC product, the PVC polymer and the plasticizer must be fully solvated or fused. The fusion or gelation temperatures

are related to the solvating strength of the plasticizer and to the size of the plasticizer molecule. Plasticizers with solubility parameters close to that of PVC require less energy to solvate or fuse the PVC polymer while larger plasticizer molecules require more thermal energy to plasticize the polymer. Esters of aromatic acids, being of greater polarity, tend to have lower fusion temperatures than the less polar esters of dicarboxylic acids. For phthalate esters, the ease of fusion decreases in the order



Table 2. Performance Properties of Selected Plasticizers^a

	Viscosity cP, 20°C	Specific gravity 20/20°	Plasticizer Efficiency		Initial Gel Temp °C ^d	Low Temp Flex. T _f , °C	Loss after aging, wt% ^e
			Shore A ^b	Ratio ^c			
General-purpose plasticizers							
Diisooheptyl phthalate (DIHP)	51	0.994	80.6	0.97	70	-23.6	19.1
Di-2-ethylhexyl phthalate (DOP)	80	0.986	81.9	1.00	71	-24.9	10.6
Diisooctyl phthalate (DIOP)	85	0.985			71		
Diisononyl phthalate (DINP)	102	0.973	83.8	1.06	80	-23.6	5.4
Di-2-ethylhexyl terephthalate (DOTP)	79	0.984	82.9	1.03		-27.7	20.4
Fast solvating Plasticizers							
Butyl benzyl phthalate (BBP)	49 ^f	1.119 ^f	79.8	0.93	58	-11.0	15.0
Diisohexyl phthalate (DHP)	37	1.008	80.4	0.97	65	-25.1	20.4
Low Temperature Plasticizers							
n-heptyl, nonyl, undecyl phthalate (711P)	49	0.972	81.7	0.98	76	-33.5	4.5
n-hexyl, octyl, decyl phthalate (610P)	34 ^f	0.971 ^f	81.7	0.98		-33.5	4.5
Di-2-ethylhexyl adipate (DOA)	15	0.927	78.5	0.93	70	-53.3	27.5
Diisononyl adipate (DINA)	22	0.922	80.6	1.16	89	-50.5	9.2
Low Volatility Plasticizers							
Diisodecyl phthalate (DIDP)	129	0.968	85.6	1.11	80	-23.6	3.0
Ditridecyl phthalate (DTDP)	322	0.957	89.5	1.26	108	-24.2	1.9
Di-n-undecyl phthalate (DUP, L11P)	77	0.954	86.3	1.14	88	-34.3	1.5
Tri-2-ethylhexyl trimellitate (TOTM)	310	0.992	86.5	1.11	85	-19.2	<1
Triisononyl trimellitate (TINTM)	430	0.978	89.7	1.24	99	-19.2	<1

^a 50 phr plasticizer except as noted

^b Shore A Hardness, 15 seconds

^c Efficiency ratio or substitution factor versus DOP

^d Determined by dynamic mechanical analysis, onset of 70 phr plastisol gelation (11)

^e weight loss after heating for 7 days at 100 °C

^f 25 °C

Plasticizer Compatibility. An important performance requirement with any plasticizer is that it must be compatible with the polymer. **Compatibility** is the ability of two or more substances to mix with each other and form a useful product. Plasticizers with solubility parameters and polarity and hydrogen bonding characteristics similar to that of the polymer, would be expected to have good compatibility. Plasticizers with greatly differing solubility parameters would have poor compatibility. When the attractive forces of either the plasticizer or the polymer are greater for themselves than for each other, the result could be exudation or spewing. Lower molecular weight phthalates such as dimethyl phthalate and diethyl phthalate are too polar to be compatible with PVC, while phthalate esters prepared from C14 and higher alcohols are too non-polar to be considered useful.

Plasticizer Permanence. Plasticizers are not permanently bound to the PVC polymer, but are free to self-associate and to associate with the polymer at differing sites. Thus under certain conditions, plasticizers can leave the flexible PVC product. The three most common mechanisms for plasticizer loss are volatilization, extraction, and migration.

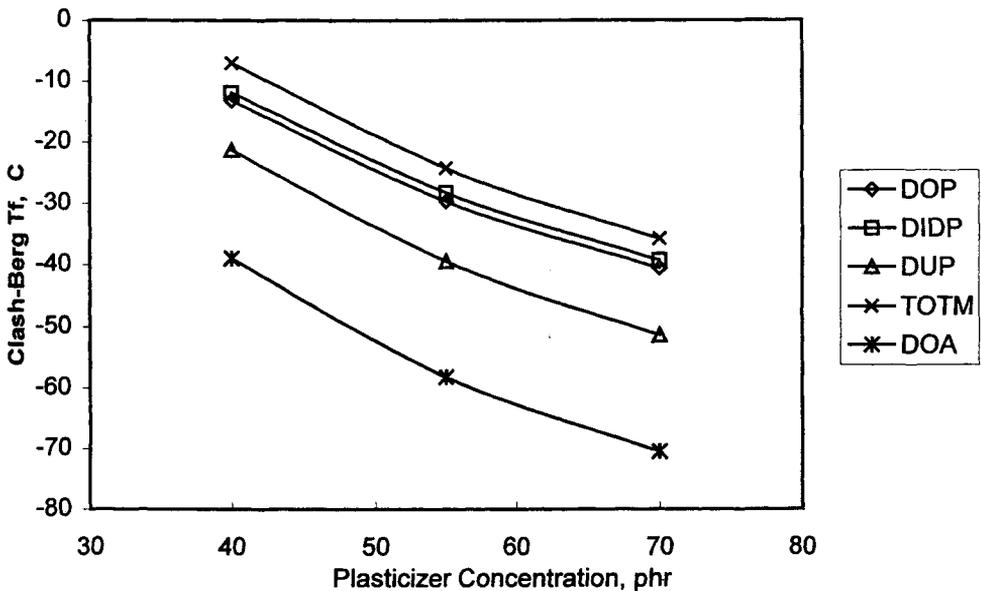
Plasticizer volatilization is directly related to the vapor pressure of the plasticizer. Volatilization losses will occur during processing and during use at elevated temperatures. Changes of as little as one carbon number of the alcohol group in a common series of esters can lead to significant reductions in losses. Trimellitate esters or polymeric plasticizers are often used to produce products designed for applications at elevated temperatures.

When plasticized PVC comes in contact with other materials, plasticizers can migrate. The rate of this migration depends both upon the structure of the plasticizer and the nature of the contact material. Plasticizers can also be extracted from PVC by a range of solvents including water. The rate of this extraction is related to the solvating strength of the solvent for the plasticizer. Water extracts plasticizers from PVC very slowly; oils are slightly more aggressive, while lower molecular weight organic solvents are very aggressive. Plasticizer molecular size is the most important factor in providing resistance to plasticizer migration or extraction. As the plasticizer molecular size increases, the tendency for plasticizer migration or extraction is reduced; polymeric plasticizers are very effective in providing migration or extraction resistance. Within a given series of esters, branched plasticizers offer better extraction and migration resistance than linear plasticizers.

Plasticizers can also migrate into other substances. Lacquer marring is controlled by the proper choice of plasticizer. Partially hydrogenated terphenyls added to DOP reduce the tendency to migrate into nitrocellulose lacquers. Terephthalate and isophthalate esters migrate to nitrocellulose slower than the corresponding ortho-phthalate esters. Migration to adhesives can destroy the cohesive nature of the adhesive. More polar plasticizers such as BBP or DHP migrate less than general-purpose plasticizers such as DOP. PVC gaskets used in either ABS or polystyrene refrigerator doors are typically prepared with polymeric plasticizers to minimize migration problems.

Low Temperature Flexibility. The addition of plasticizer to a PVC product extends the lower useful temperature limit of the finished product. Generally, the lower temperature limit is enhanced as the plasticizer concentration is increased. However some plasticizers are more effective at this than others. The low temperature flexibility of the finished product results from depression of the polymer's Tg by the plasticizer. Low polarity plasticizers that lack aromatic moieties have more degrees of rotational freedom than their higher polarity counterparts of similar molecular weight. Thus, aliphatic diesters of adipic, azelaic, and sebacic acids are very effective in improving the low temperature performance of flexible PVC. A major contribution to low temperature performance is also realized from the alcohol portion of the esters; the greater the linearity of the plasticizer, the greater the low temperature performance. For flexible PVC, the torsion modulus method of Clash-Berg and the Bell brittleness temperatures are commonly used. The low temperature flexibility for PVC plasticized with several esters is shown in Figure 4.

Figure 4. Low Temperature Effects in Plasticized PVC



Flame Resistance. Rigid PVC is inherently fire resistant and self-extinguishing; however the addition of plasticizers such as phthalates, adipates, and trimellitates contributes to flammability. The triaryl and alkylaryl phosphates and brominated phthalate plasticizers inhibit burning of plasticized PVC. These products are often blended with other plasticizers to achieve a balance of flame resistance, physical

properties, and cost. Chlorinated paraffins can also be used as secondary plasticizers, to help reduce flammability and smoke; however high volatility and potential compatibility problems restricts their use to but a few end uses. Flame resistance or smoke suppression may also be gained through addition of various additives into the flexible PVC formulation. These additives include antimony trioxide, alumina trihydrate, molybdenum ammonium octanoate, and zinc borate.

Plastisol Viscosity. In the processing of plastisols, plastisol viscosities at shear rates associated with the manufacturing process technology and plastisol viscosity stability are important properties. Using lower molecular weight or linear plasticizers will yield lower plastisol viscosity when compared at equal concentrations. However once the formulations are adjusted for equal hardness by taking into account the efficiency differences of the plasticizers, less-efficient plasticizers will often yield equal or lower plastisol viscosities, as they require higher plasticizer levels to achieve the same hardness. For example, even though DOP gives a lower plastisol viscosity than DINP at the same concentration, at equal hardness formulations, the DINP based plastisol would have the lower viscosity.

Plastisols are often mixed and stored before use. In this case, it is of great importance for the plasticizer to show little or no viscosity increase upon storage at room temperature. Plastisol viscosity for BBP based plastisols will increase significantly upon storage, while plastisols prepared with less polar plasticizers such as DINP and DIDP will remain relatively stable for some time. For phthalate esters, plastisol viscosity stability generally follows the order

DIDP > DINP > DOP > DHP > BBP.

Volume Costs. Most finished plastic products or articles are sold by the unit or by volume; however the raw materials used to prepare the product are purchased and formulated by weight. Thus when the costs to prepare the product are calculated, it should be determined on a cost per unit or cost per volume basis. Ingredients with lower specific gravities will give an increase in the number of units and thus plasticizers with lower specific gravities will yield lower costs per unit or lower volume costs.

Plasticizer efficiency is also important in determining volume costs. The volume costs for PVC polymer are higher than the volume cost of the plasticizers because of the high specific gravity of the polymer. Thus as more of the lower-volume-cost plasticizers are added to the polymer, the volume costs of the finished product decrease. Less efficient plasticizers require higher levels of addition to achieve the same degree of hardness or tensile properties; thus less efficient plasticizers lead to lower volume costs. For example when comparing the volume costs of a DOP plasticized product to the volume costs of the same article prepared with DINP at the same Shore A hardness, the DINP product will have lower volume costs because of the lower specific gravity of the DINP and the reduced efficiency.

Plasticizer Selection for Specific Applications

Plasticizer selection involves trying to meet a combination of end use performance requirements, processing needs, cost, and in some cases, specific regulatory requirements. Products produced from flexible PVC are used in a wider range of applications and industry market segments, than any other polymeric system. Table 2 lists a breakdown of the usage of plasticizers by different market segments.

Flexible PVC products are produced by a wide variety of differing manufacturing technologies. There are two main process routes to producing plasticized PVC products, melt processing and plastisol processing. In melt processing, suspension-grade PVC polymer, plasticizers, stabilizers, fillers, and other additives are compounded at elevated temperatures. The compound can be further shaped into final form using calendering, extrusion, or injection molding techniques.

The melt processing process often begins with formation of a **dry blend**. As the plasticizer and the polymer and other additives are mixed under shear, the plasticizer is slowly absorbed by the porous polymer particles. With continued mixing, the temperature of the mix will increase and eventually yield a dry powder. This powder can be stored, compounded into pellets, directly extruded into a finished product, or fed to a Banbury mixer or mill and then calendered. Plasticizer selection does impact the dry blending process. Plasticizers with lower viscosities will dry blend faster than higher viscosity plasticizers (12). Higher viscosity plasticizers such as trimellitate esters and heavier phthalate esters are often preheated prior to the dry blending step to reduce the time required to complete the dry blending step.

Plastisols are liquid dispersions formed by mixing emulsion-grade PVC polymer into the liquid plasticizer system. Fillers, stabilizers, and other additives are also added, as needed. Plastisols are mixed and shaped at relatively low temperatures. After shaping, the temperature is raised to form the fused plasticized products. Plastisol shaping techniques include rotomolding, spread coating, dipping, pouring, and extrusion. Often plasticizers are chosen more for the benefits they bring to the plastisol manufacturing process, for example in reduced fusion temperature, reduced volatility, or improved viscosity stability, than for product end use performance.

The largest market sector for plasticizers is the film, sheet, and coated fabric market sector. These products are manufactured by calendering, extrusion, cast films, and spread coating processes and are used to produce a wide variety of products including table cloths, swimming pool liners, tarpaulins, agriculture films, wall coverings, shower curtains, upholstery fabrics, and shoe fabrics. The majority of these products will use the general-purpose plasticizers DOP and DINP. Specialty plasticizers are often used to improve performance attributes. For example, DIDP is used to make a product last longer and to improve the extraction resistance. Linear phthalate esters such as linear dinonyl phthalate (L9P) or linear diundecyl phthalate (DUP) are used for improved UV resistance, and fast fusing plasticizers (BBP, DHP) to help improve the processability in spread coating. Adipate esters (DOA, DINA) can be added to the phthalate esters in other film and sheet products to improve the low temperature performance.

Table 3. Plasticized PVC Major Market Segments^a

Film, Sheet, and Coated Fabrics	31 %
Wire and Cable	24 %
Molding and Extruded products	17 %
Flooring	14 %
Adhesives, sealants, coatings, inks	5 %
Food, medical, other regulated	3 %
Other miscellaneous	6 %

Another large end use for flexible PVC is wire and cable. With electrical cables, plasticizer selection is dependent upon the performance specifications of the insulation material and the jacketing. Higher temperature rated products require more permanent plasticizers. In the US, building wire is typically formulated with trimellitate plasticizers such as TOTM or TINTM. Often to reduce costs, heavier phthalates such as DTDP or DUP are blended with the trimellitates. In other parts of the world where the performance requirements for building wire are not as severe, general purpose plasticizers can be used, but the trend remains to use higher molecular weight plasticizers such as DIDP to improve product performance.

Cushion vinyl flooring is prepared by coating a substrate with various layers of plastisols. These products generally use a mixture of general-purpose plasticizers such as DIHP, DOP, and DINP often in blends with DHP or BBP. These faster fusing plasticizers improve processability and stain resistance of the finished flooring product. Vinyl floor tiles and other sheet flooring are produced by calendaring; again general-purpose plasticizers, often used in blends with fast fusing plasticizers, are commonly used. Plasticized PVC is also a major component of some types of carpets and carpet tiles, either as an adhesive or as a backing material. Faster fusing plasticizers such as DIHP offer advantages over DOP because of the lower fusion temperature, which is desirable to protect the carpet fibers.

Most molded and extruded products are prepared from general purpose plasticizers such as DOP and DINP, as these products offer the best compromise between price and performance. Products designed for outdoor applications will often use more permanent plasticizers such as DIDP. Often choice of regulatory requirements will dictate plasticizer choice. Molded medical devices will use DOP while DINP will be the plasticizer of choice for toys. Molded products used for automotive interiors will use heavier phthalates such as DIDP or DUP to meet automotive manufacturer fog performance requirements.

In addition to these major market segments, plasticizers are used in a variety of smaller segments. Adhesives and sealants generally use lower molecular weight phthalate esters because of improved solvency and lower fusion temperatures. One major use of plasticized PVC is automotive underbody coating; these products are highly filled plastisols that are mostly commonly based upon DIHP, DOP, or DINP.

Another important use of plasticizers is to produce vinyl Medical devices. Most of these products use DOP although DINP is used for vinyl examination gloves.

Plasticizers for Other Polymers

Polymers other than PVC account for less than 10% of the current world wide plasticizer usage. While the combination of PVC polymer, plasticizers, and other additives can yield an extensive range of flexible products with varying performance characteristics, plasticizer usage with other polymers does not produce the same range of versatility. More often plasticizers are used with other polymer systems more for processing improvements than for producing flexible products.

Plasticizers are used with acrylic polymers to produce flexible coatings, caulks, and sealants. Most of the common phthalates and adipates have been described as having some compatibility with acrylic systems, although the number of plasticizers having acceptable performance is smaller than those listed for PVC. The most common plasticizers used are BBP, DBP, DHP, DIHP, and certain benzoate esters.

Polyvinyl acetate (PVAc) emulsion polymers are used for adhesives, sealants, and paints. PVAc homopolymer is too brittle for most end uses, so much of the PVAc used in the paint industry is internally plasticized through the incorporation of comonomers into the polymer backbone. Externally plasticized PVAc is used in adhesives. The most common plasticizers used with adhesives are the dibutyl phthalates and benzoate esters.

Nylon is a highly crystalline material and, as such, plasticization can only occur at very low levels. Plasticizers used with nylon are typically sulfonamides, as these products are significantly more compatible with nylon than are phthalates. Sulfonamides can be used as nylon flow aids, to retard degradation and to speed up processing.

Many rubbers and elastomers are comprised of long hydrocarbon segments, and thus can accept petroleum oils and other predominately hydrocarbon products for use as plasticizer or extenders. These products are available at a significantly lower cost than the synthetic ester plasticizers. Phthalates and adipates of linear alcohols are used to enhance low temperature properties of certain rubber applications, which cannot be met using the hydrocarbon extenders. Polar elastomers such as nitrile rubber and polychloroprene have low compatibility with hydrocarbons and require more polar products such as phthalates or adipates.

Plasticized polyvinyl butyral (PVB) is used as a laminating film between layers of glass to provide strength and shatter resistance. This forms the "safety" glass used in automobile windshields and architectural glass. PVB can be plasticized with a variety of esters, but in practice only a few products are used as the plasticizer selection is a complicated process. The most common plasticizers used with PBV in safety glass are di-n-hexyl adipate and the di-n-heptanoic acid esters of tri- or tetra-ethylene glycol. These esters give excellent compatibility, clarity, and resistance to sunlight.

Many cellulosic materials, including cellulose nitrate are compatible with relatively high levels of plasticizers. Plasticizers are used to reduce processing temperatures, improve impact resistance, and to increase flexibility and resistance to

cracking in these materials. Cellulose acetate can be plasticized with more polar esters such as dimethyl and diethyl phthalate. Cellulose nitrate, on the other hand, shows better compatibility with BBP and dibutyl or other heavier phthalates.

Plasticizers can be used to reduce both the viscosity and the cost of polyurethane and polysulfide automotive and construction sealants. Higher molecular weight phthalate esters such as DINP, DIDP, and DUP are generally suitable for most polyurethane sealant applications. Polysulfide sealants require more polar plasticizers such as the alkyl benzyl phthalates. For automotive interior applications, the low fog requirements generally excludes the use of the more volatile polar plasticizers such as BBP. In those cases, higher molecular weight polar products such as Texanol® benzyl phthalate can be used.

Diluents or plasticizers for epoxy resins lower the viscosity of the uncross-linked resin for greater ease in application of surface coatings and adhesives. Non-reactive plasticizers such as phthalates and phosphates will reduce the viscosity but lead to poor impact resistance and lower the extraction resistance. Reactive plasticizers are low molecular weight epoxy compounds, typically having one reactive epoxy group per molecule. These contribute to lengthening the polymer segments between cross-links and produce a slight softening and flexibility effect with impaired impact strength. The products used include butyl glycidyl ether and the glycidyl esters of neodecanoic acid.

Health Aspects of Plasticizers (13)

Toxicity. The toxicity of a substance is a measure of its effects on living organisms. It is not possible to simply state whether or not plasticizers or any other substances are toxic, because this is determined by the dose. The acute toxicity of a substance is an assessment of the effect that a single dose will have upon a living organism. The relevant parameter is the dose that is lethal for 50% of the test animals, expressed relative to the body weight (LD_{50}). The acute toxicity of phthalate and adipate esters is extremely low; in fact lower than that found for common everyday substances such as ethyl alcohol and common table salt.

Chronic toxicity describes the effects that take place on a living organism as a consequence of long term exposure. Some phthalate esters were shown to cause increased liver tumors in rats and mice when these animals were fed phthalates at very high levels (comparable to human consumption of 300 g DOP per day). More recent studies have shown that phthalates are not genotoxic; plasticizers do not interact with genetic material. Other studies have shown that while oral administration of plasticizers to rodents causes increases in microbodies in the liver called peroxisomes, administration of the same plasticizers to non-rodent species such as marmosets does not lead to peroxisome proliferation and liver damage.

Phthalates are also alleged to be endocrine disrupters, with the capability to produce changes in the hormone system, which can lead to reproductive problems. Definitive studies have shown that the major commercial phthalate esters are not estrogenic (14) while other studies suggest that DINP, and DIDP are not endocrine disrupters. Recently the health risks associated with flexible PVC products was examined by an independent panel of scientists led by Dr. C. E. Koop, former US

Surgeon General. This panel concluded that products plasticized with DOP and DINP are not harmful(15).

The level of human exposure to plasticizers. Experimental investigations and assessments in the USA and in Europe have shown that the average human intake of plasticizer amounts to only 2 g per person per year. This is mostly due to traces of DOA migrating from food packaging. The so-called No Observed Effect Level (NOEL) for DOA and DOP in rodents is around 40 mg per kg body weight per day or higher. Extrapolating this to the average human, this would equate to at least 1000 g plasticizer per person per year. This is a 500 fold safety factor between estimated plasticizer and the No Observed Effect Levels. If the differences in responses between rodents and primates are considered, the safety factor is even greater.

Plasticizers in the Environment. The release of plasticizers into the environment can occur during manufacture and distribution of the plasticizer, during fabrication of the flexible PVC product, from plasticizer loss during the use of the product or after its disposal. Plasticizer losses during production and distribution are tightly controlled and are very small. Plasticizers are very insoluble in water and thus plasticizer releases during product use or disposal are minimal. Most plasticizer releases into the environment occur by evaporation during the processes required to incorporate the plasticizer into the PVC polymer. Plasticizer losses by this mechanism are continually being reduced by the installation of incinerators, scrubbing, and filtration equipment and by switching to less volatile plasticizers. For example, fusion oven studies have shown that by replacement of DOP with DINP, the plasticizer emission can be reduced by almost 50%. There are no indications of an accumulation of plasticizers in water, soil, or air because they biologically and photochemically degrade. Degradation is particularly rapid under aerobic conditions to produce carbon dioxide and water.

Future of Plasticizers

The future of plasticizers is tied closely to the future of PVC. In recent years, several environmental activist groups have criticized PVC because it contains chlorine and a mistaken belief that the production, use, and disposal of PVC products caused serious damage to the environment. Although the initial attacks were relatively unsuccessful, it has raised awareness of alternative materials that could replace flexible PVC in some applications.

Recently, the environmental focus has shifted towards additives used in PVC; metal stabilizers and plasticizers. Plasticizers are criticized because under certain conditions, small amounts can migrate from the flexible PVC product. The future of plasticizers is strongly dependent on the continued availability of cost-effective plasticizers that do not present unacceptable health and environmental risks.

Up to now this demand has been met with the three primary plasticizers, DOP, DINP, and DIDP. As discussed, higher molecular weight phthalates are more permanent, have lower water solubility, and migrate slower than lower molecular weight products. It is expected that the trend of replacing DOP with either DINP or DIDP will

continue, perhaps at accelerated rates. In the absence of any specific environmental or health drivers or new regulations, it is not expected that any new plasticizers or new plasticizer technology will be developed to replace sizable volumes of these plasticizers in the near future.

One consequence of the emotive attacks on flexible PVC, is that product designers will express interest in non-PVC products while producers of competitive flexible polymer systems will promote their products using the perceived negative PVC attributes. Flexible PVC products still offer cost, processing, and performance advantages over potential replacement systems; however, it is expected that future developments will bring forth new polymers which will begin to slowly replace flexible PVC in selected applications.

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