

PLASTICIZERS

A plasticizer is a substance the addition of which to another material makes that material softer and more flexible. This broad definition encompasses the use of water to plasticize clay for the production of pottery, and oils to plasticize pitch for caulking boats. A more precise definition of plasticizers is that they are materials which, when added to a polymer, cause an increase in the flexibility and workability, brought about by a decrease in the glass-transition temperature, T_g , of the polymer. The most widely plasticized polymer is poly(vinyl chloride) (PVC) due to its excellent plasticizer compatibility characteristics, and the development of plasticizers closely follows the development of this commodity polymer. However, plasticizers have also been used and remain in use with other polymer types.

The amount of plasticizer added to the polymer in question varies, depending on the magnitude of the effect required. For example, a small addition of plasticizer may be made simply to improve the workability of the polymer melt. This contrasts with larger additions made with the specific intention of completely transforming the properties of the product. For example, PVC without a plasticizer, ie, unplasticized PVC (PVC-U), is used in applications such as pipes and window profiles; with plasticizer added, articles such as PVC food film, PVC cable insulation, and sheathing and PVC floorings are formed.

There are presently ~300 plasticizers in manufacture. Of these ~100 are of commercial importance. A list of some common commodity and speciality plasticizers are given in Table 1.

1. Types of Plasticizers

Two principle methods exist for softening a polymer to bring about the dramatic effects of plasticization. A rigid polymer may be internally plasticized by chemically modifying the polymer or monomer so that the flexibility of the polymer is increased. Alternatively, a rigid polymer can be externally plasticized by the addition of a suitable plasticizing agent, ie, by preparing a product consisting of a resin and a plasticizer. The external plasticizing route is the more common principally because of lower overall costs and also the fact that the use of external plasticizers allows the fabricator of the final article a certain degree of freedom in devising formulations for a range of products.

1.1. Internal Plasticizers

There has been much dedicated work on the possibility of internally plasticized PVC. However, in achieving this by copolymerization significant problems exist: (1) the affinity of the growing polymer chain for vinyl chloride rather than a comonomer implies that the incorporation of a comonomer into the chain requires significant pressure; (2) since the use of recovered monomer in PVC production is standard practice, contamination of vinyl chloride with comonomer in this respect creates additional problems; and (3) the increasing complexity of the reaction can lead to longer reaction times and hence increased costs. Thus, since standard external plasticizers are relatively cheap they are normally preferred.

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Table 1. Plasticizers^a In Common Use

Plasticizer	Abbreviation	Alcohol carbon num- ber	Alcohol	CAS Registry Number	M _w	Density at 20°C, g/cm ³
<i>Phthalates</i>						
diisobutyl phthalate	DIBP	4	isobutyl alcohol	[84-69-5]	278.3	1.039
dibutyl phthalate	DBP	4	butanol	[84-74-2]	278.3	1.046
diisooheptyl phthalate	DIHP	7	isoheptyl alcohol	[41451-28-9] [71888-89-6]	362	0.991
L7,9-phthalate	L79P; 79P	7,9	linear heptanol, nonanol	[68515-41-3]	380	0.985
L7,11-phthalate	L711P; 711P	7,11	linear heptanol, undecanol	[68648-91-9]	414	0.971
di-2-ethylhexyl phthalate ^b	DEHP	8	2-ethylhexanol	[117-81-7]	390	0.984
diisooctyl phthalate	DIOP	8	isooctyl alcohol	[27554-26-3]	390	0.983
dinonyl phthalate	DNP	9	nonanol (3,5,5-trimethylhexanol)	[87-76-4]	419	0.97
diisononyl phthalate	DINP	9	isononyl alcohol	[28553-12-0] [68515-48-0]	419	0.975
diisodecyl phthalate	DIDP	10	isodecyl alcohol	[68515-49-1]	447	0.967
L9,11-phthalate	L911P; 911P	9,11	linear nonanol, undecanol	[68515-43-5]	454	0.96
diundecyl phthalate	DUP	11	undecanol	[3648-20-2]	474	0.953
diisoundecyl phthalate	DIUP	11	isoundecyl alcohol	[85507-79-5]	474	0.962
undecyldodecyl phthalate	UDP	11,12	undecanol, dodecanol		488	0.957
diisotridecyl phthalate	DTDP	13	isotridecyl alcohol	[27253-26-5] [68515-47-9]	531	0.952
benzylbutyl phthalate	BBP	4,7	butanol, benzyl chloride	[85-68-7]	312.3	1.119
<i>Adipates</i>						
di-2-ethylhexyl adipate ^c	DEHA	8	2-ethylhexanol	[103-23-1]	370.6	0.929
diisononyl adipate	DINA	9	isononyl alcohol	[33703-08-1]	398	0.929
diisodecyl adipate	DIDA	10	isodecyl alcohol	[27178-16-1]	427.1	0.915
<i>Trimellitates</i>						
tris-2-ethylhexyl trimellitate ^d	TOTM	8	2-ethylhexanol	[3319-31-3]	530	0.991
L7,9-trimellitate	L79TM	7,9	linear heptanol, nonanol	[68515-60-6]	530	0.996
L8,10-trimellitate	L810TM	8,10	linear octanol, decanol	[67989-23-5]	592	0.973
<i>Phosphates</i>						
tri-2-ethylhexyl phosphate ^e	TOP	8	2-ethylhexanol	[78-42-2]	434	0.926
2-ethylhexyl diphenyl phosphate	DPOP	6,8	phenol, 2-ethylhexanol	[1241-94-7]	362.4	1.091
tricresyl phosphate	TCP	7	methylphenol	[1330-78-5]	368.2	1.165

^aEsters made from the reaction of acids (or anhydrides) with alcohols. 1-Alkanols produce linear chains, hence the L designation in plasticizer names.

^bOften dioctyl phthalate (DOP).

^cAlso dioctyl adipate (DOA).

^dAlso trioctyl trimellitate (TOTM).

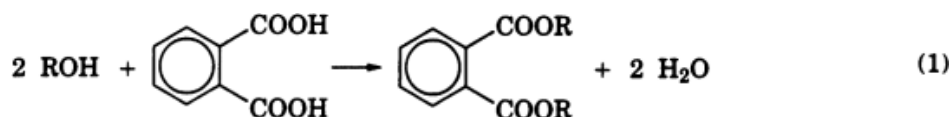
^eAlso trioctyl phosphate (TOP).

1.2. External Plasticizers

There are two distinct groups of external plasticizers. A primary plasticizer, when added to a polymer, causes the properties of elongation and softness of the polymer to be increased. These changes are brought about by mechanisms described below. A secondary plasticizer, when added to the polymer alone, does not bring about these changes and may have limited compatibility with the polymer. However, when added to the polymer in combination with a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer. For this reason secondary plasticizers are also known as extenders.

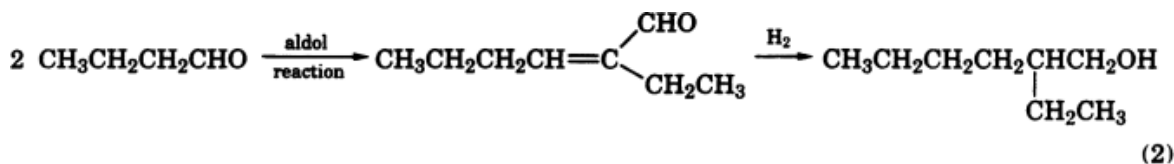
1.3. Commodity Phthalate Esters

The family of phthalate esters are by far the most abundantly produced worldwide. Both orthophthalic and terephthalic acid and anhydrides are manufactured. The plasticizer esters are produced from these materials by reaction with an appropriate alcohol (eq. 1); terephthalate esterification for plasticizers is performed more abundantly in the United States. Phthalate esters are manufactured from methanol (C_1) up to C_{17} alcohols, although phthalate use as PVC plasticizers is generally in the range C_4 to C_{13} . The lower molecular weight phthalates find use in nitrocellulose; the higher phthalates as synthetic lubricants for the automotive industries.



1.3.1. Di-2-Ethylhexyl Phthalate

In Western Europe, di-2-ethylhexyl phthalate [117-81-7] (DEHP), also known as dioctyl phthalate (DOP), accounts for about 50% of all plasticizer usage and as such is generally considered as the industry standard. The reason for this is that it is in the mid-range of plasticizer properties. DEHP (or DOP) is the phthalate ester of 2-ethylhexanol, which is normally manufactured by the dimerization of butyraldehyde (eq. 2), the butyraldehyde itself being synthesized from propylene (see Butyraldehydes).

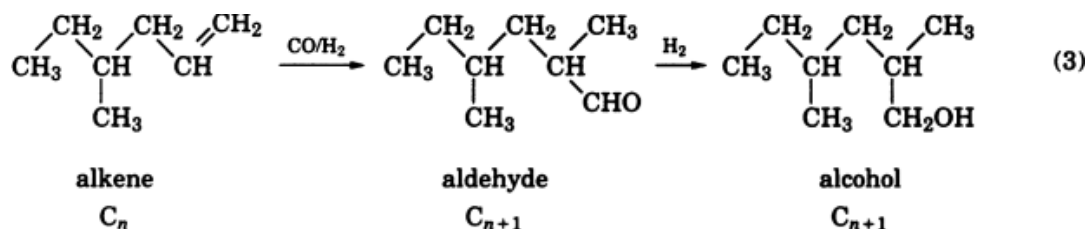


The widespread sales of this plasticizer are a reflection of its all-around plasticizing performance and its provision of adequate properties for a great many standard products. It possesses reasonable plasticizing efficiency, fusion rate, and viscosity which, coupled with the normally competitive price, go a long way to explaining the popularity of this plasticizer. Some concerns have been periodically raised as to the possible toxicity of this material, but it can be said that these concerns are often related to the vast and widespread study of the toxicity of DEHP.

1.3.2. Diisononyl Phthalate and Diisodecyl Phthalate

These primary plasticizers are produced by esterification of oxo alcohols of carbon chain length nine and ten. The oxo alcohols are produced through the carbonylation of alkenes (olefins). The carbonylation process (eq. 3) adds a carbon unit to an alkene chain by reaction with carbon monoxide and hydrogen with heat, pressure, and catalyst. In this way a C_8 alkene is carbonylated to yield a C_9 alcohol; a C_9 alkene is carbonylated to produce a C_{10} alcohol. Due to the distribution of the $\text{C}=\text{C}$ double bond in the alkene and the varying effectiveness of certain catalysts, the position of the added carbon atom can vary and an isomer distribution is generally created in such a reaction; the nature of this distribution depends on the reaction conditions. Consequently these alcohols are termed iso-alcohols and the subsequent phthalates iso-phthalates, an unfortunate designation in view of possible confusion with esters of isophthalic acid.

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The C₉ and C₁₀ iso-phthalates (DINP and DIDP) generally compete with DEHP as commodity general-purpose plasticizers. Other iso-phthalates are available at opposite ends of the carbon number range (eg, diisooheptyl phthalate (DIHP), C₇, and diisotridecyl phthalate (DTDP), C₁₃), but these serve more speciality markets. The C₈ iso-phthalate, diisooctyl phthalate (DIOP), has also had traditional sales in the commodity plasticizer markets where it is seen as an equivalent to DEHP.

1.4. The Specialty Plasticizers

For the purpose of this article, the term specialty plasticizer refers to any plasticizer other than DEHP (DOP), DIOP, DINP, or DIDP.

1.4.1. Specialty Phthalates

These comprise the fast-fusing, low carbon number phthalates dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), benzylbutyl phthalate (BBP), and diisooheptyl phthalate (DIHP); the low volatility iso-phthalates diisoundecyl phthalate (DIUP) and diisotridecyl phthalate (DTDP); and also the linear and semilinear phthalates for low viscosity applications, eg, L911P and L1012P. In each case these materials are the phthalate esters of alcohols of varying chain length.

1.4.2. Adipate Esters

Alcohols of similar chain length to those used in phthalate manufacture can be esterified with adipic acid rather than phthalic anhydride to produce the family of adipate plasticizers. For example, esterification of 2-ethylhexanol with adipic acid yields di-2-ethylhexyl adipate (DEHA), also known as dioctyl adipate (DOA). The family of adipic acid esters in PVC applications has the significant properties of improved low temperature performance relative to phthalates and lower plastisol viscosities in plastisol applications, due to the lower inherent viscosities of the plasticizers themselves. Adipates used are typically in the C₈ to C₁₀ range; incompatibility problems can be encountered at higher carbon numbers, especially at high addition levels. Relative to phthalates, adipates suffer from higher volatilities and higher migration rates, and because they are a specialty for the PVC industry, higher prices. As a result, it is not uncommon to observe adipates used in blends with phthalates to produce a compromise of properties.

1.4.3. Trimellitate Esters

These materials are produced by the esterification of a range of alcohols with trimellitic anhydride (TMA), which is similar in structure to phthalic anhydride with the exception of the third functionality (COOH) on the aromatic ring. Consequently, esters are produced in the ratio of three moles of alcohol to one mole of anhydride. Common esters in this family are tris-2-ethylhexyl trimellitate (trioctyl trimellitate, TOTM); L79TM, an ester of mixed semilinear C₇ and C₉ alcohols; and L810TM, an ester of mixed linear C₈ and C₁₀ alcohols.

The principal feature of these esters, when processed with PVC, is their low volatility, and consequently large volumes of trimellitate esters are used in high specification electrical cable insulation and sheathing. The extraction and migration resistance of these materials are also significantly improved relative to the phthalates. The low volatile loss figures also result in usage in automotive interior applications where the

issue of windscreen fogging is important. In this respect they often compete with the linear high molecular weight phthalates such as 911P.

1.4.4. *Phosphate Esters*

The principal advantage of phosphate esters is the improved fire retardancy relative to phthalates. The fire performance of PVC itself, relative to other polymeric materials, is very good due to its high halogen content, but the addition of plasticizers reduces this. Consequently there is a need, in certain demanding applications, to improve the fire-retardant behavior of flexible PVC.

Tris(2-ethylhexyl) phosphate shows good compatibility with PVC and also imparts good low temperature performance in addition to good fire retardancy. 2-Ethylhexyl diphenyl phosphate has widespread use in flexible PVC applications due to its combination of properties of plasticizing efficiency, low temperature performance, migration resistance, and fire retardancy.

1.4.5. *Sebacate and Azelate Esters*

Esters produced from 2-ethylhexanol and higher alcohols with linear aliphatic acids are used in some demanding flexible PVC applications where superior low temperature performance is required. Di-2-ethylhexyl sebacate (DOS) and di-2-ethylhexyl azelate (DOZ) are the most commonly used members of this group, but diisodecyl sebacate (DIDS) is also encountered. They give superior low temperature performance to adipates but also command a significant premium, and their usage is generally limited to extremely demanding low temperature flexibility specifications, eg, underground cable sheathing in arctic environments.

1.4.6. *Polyester Plasticizers*

These materials have found widespread use due to their exceedingly low volatility and high resistance to chemical extraction. Polyester plasticizers are based on condensation products of propanediols or butanediols with adipic acid or less commonly phthalic anhydride. The growing polymer chain may then be end-capped with an alcohol or monobasic acid, although nonend-capped polyester plasticizers can be produced by strict control of the reaction stoichiometry. Because of their higher molecular mass compared to other plasticizers, these materials have exceedingly high viscosities, ca 3–10 Pas (30–100 P), which can in some cases cause processing problems in dry blending and plastisol applications.

1.4.7. *Sulfonate Esters*

These are marketed as efficient and easily processible plasticizers with good resistance to extraction. They are typically aryl esters of a C₁₃ to C₁₅ alkanesulfonic acid.

1.5. *Secondary Plasticizers*

Also known as extenders, secondary plasticizers continue to play a significant role in flexible PVC formulations. They do not impart flexibility to the PVC resin alone, but when combined with a primary plasticizer act in such a way as to add flexibility to the final product. The majority of secondary plasticizers in use are chlorinated paraffins, which are hydrocarbons chlorinated to a level of 30–70%. For a given hydrocarbon chain, viscosity increases with chlorine content, as does the fire retardancy imparted to the formulation. These materials aid fire retardancy due to their chlorine content. Chlorinated paraffins of the same chlorine content may, however, have different volatilities and viscosities if they are based on different hydrocarbon chains (see Chlorocarbons and chlorohydrocarbons, chlorinated paraffins).

As well as imparting improved fire retardancy these materials may also result in volume cost savings if they can be purchased for a lower price than the commodity phthalate. Precise knowledge of the compatibility between standard plasticizers and chlorinated paraffins is required because some mixtures become incompatible with each other and the PVC resins in use at certain temperatures. Phthalate–chlorinated

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paraffin compatibility decreases as the molecular mass of the phthalate and the plasticizer content of the PVC formulation increase. Many compatibility graphs are available (1).

Other materials that are often referred to as secondary plasticizers include materials such as epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO) and similar materials. These can act as lubricants but also as secondary stabilizers to PVC due to their epoxy content which can remove HCl from the degrading polymer.

2. The Mechanism of Plasticizer Action

This discussion refers to external plasticization only. Several theories, varying in detail and complexity, have been proposed in order to explain plasticizer action. Some theories involve detailed analysis of polarity, solubility, and interaction parameters and the thermodynamics of polymer behavior, whereas others treat plasticization as a simple lubrication of chains of polymer from each other, analogous to the lubrication of metal parts by oil. Although each theory is not exhaustive, an understanding of the plasticization process can be gained by combining ideas from each theory, and an overall theory of plasticization must include all these aspects.

The steps involved in the incorporation of a plasticizer into a PVC product can be divided into five distinct stages:

- (1) Plasticizer is mixed with PVC resin.
- (2) Plasticizer penetrates and swells the resin particles.
- (3) Polar groups in the PVC resin are freed from each other.
- (4) Plasticizer polar groups interact with the polar groups on the resin.
- (5) The structure of the resin is re-established, with full retention of plasticizer.

Steps 1 and 2 can be described as physical plasticization, and the precise details of how this is carried out depends on the applications technology involved, ie, suspension or paste PVC. The rate at which step 2 occurs depends on the physical properties of plasticizer viscosity, resin porosity, and particle size.

Steps 3 and 4, however, can be described as chemical plasticization since the rate at which these processes occur depends on the chemical properties of molecular polarity, molecular volume, and molecular weight. An overall mechanism of plasticizer action must give adequate explanations for this as well as the physical plasticization steps.

The importance of step 5 cannot be stressed too strongly, since no matter how rapidly and easily steps 1–4 occur, if plasticizer is not retained in the final product the product will be rendered useless. For many polymers, steps 1–4 proceed adequately but the plasticizer is not retained in the final product, leading to a product which is unacceptable.

2.1. The Lubricity Theory

This is based on the assumption that the rigidity of the resin arises from intermolecular friction binding the chains together in a rigid network. On heating, these frictional forces are weakened so as to allow the plasticizer molecules between the chains. Once incorporated into the polymer bulk the plasticizer molecules shield the chains from each other, thus preventing the reformation of the rigid network. Although attractive in its simplicity, the theory does not explain the success of some plasticizers and the failure of others.

2.2. The Gel Theory

This extends the lubricity theory in that it deals with the idea of the plasticizer acting by breaking the resin–resin attachments and interactions and by masking these centers of attachment from each other, preventing their reformation. Such a process may be regarded as necessary but again by itself is insufficient to explain a completely plasticized system, because although a certain concentration of plasticizer molecules provides plasticization by this process, the remainder act more in accordance with the lubricity theory, with unattached plasticizer molecules swelling the gel and facilitating the movement of plasticizer molecules, thus imparting flexibility. Molecules acting by this latter action may, on the basis of molecular size measurements, constitute the bulk of plasticizer molecules. If plasticization took place solely by this method it would not be possible to explain the ability of PVC resins to accept their own weight in plasticizer without exudation, ie, large amounts of additional space (free volume) are created which other plasticizer molecules can occupy.

2.3. The Free Volume Theory

This extends the lubricity and gel theories and also allows a quantitative assessment of the plasticization process.

The free volume, V_f , of a polymer is described by the equation $V_f = V_t - V^0$ where V_t = specific volume at a temperature t and V^0 = specific volume of an arbitrary reference point, usually taken as zero degrees Kelvin. Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. A rigid resin, eg, unplasticized PVC, is seen to possess very little free volume whereas resins which are flexible in their own right are seen as having relatively large amounts of free volume. Plasticizers therefore act so as to increase the free volume of the resin and also to ensure that free volume is maintained as the resin–plasticizer mixture is cooled from the melt. Combining these ideas with the gel and lubricity theories, it can be seen that plasticizer molecules not interacting with the polymer chain must simply fill free volume created by those molecules that do. These molecules may also be envisaged as providing a screening effect, preventing interactions between neighboring polymer chains thus preventing the rigid polymer network from reforming on cooling.

For the plasticized resin, free volume can arise from motion of the chain ends, side chains, or the main chain. These motions can be increased in a variety of ways, including increasing the number of end groups, increasing the length of the side chain, increasing the possibility of main group movement by the inclusion of segments of low steric hindrance and low intermolecular attraction, introduction of a lower molecular weight compound which imparts the above properties, and raising the temperature.

The introduction of a plasticizer, which is a molecule of lower molecular weight than the resin, has the ability to impart a greater free volume per volume of material because there is an increase in the proportion of end groups and the plasticizer has a glass-transition temperature, T_g , lower than that of the resin itself. A detailed mathematical treatment (2) of this phenomenon can be carried out to explain the success of some plasticizers and the failure of others. Clearly, the use of a given plasticizer in a certain application is a compromise between the above ideas and physical properties such as volatility, compatibility, high and low temperature performance, viscosity, etc. This choice is application dependent, ie, there is no ideal plasticizer for every application.

2.4. Solvation–Desolvation Equilibrium

From the observation of migration of plasticizer from plasticized polymers it is clear that plasticizer molecules, or at least some of them, are not bound permanently to the polymer as in an internally plasticized resin, but rather an exchange–equilibrium mechanism is present. This implies that there is no stoichiometric relationship

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between polymer and plasticizer levels, although some quasi-stoichiometric relationships appear to exist (3, 4). This idea is extended later in the discussion of specific interactions.

2.5. Generalized Structure Theories and Antiplasticization

In their simplest form these theories attempt to produce a visual representation of the mechanism of plasticizer action (1, 5, 6). The theories are based on the concept that if a small amount of plasticizer is incorporated into the polymer mass it imparts slightly more free volume and gives more opportunity for the movement of macromolecules. Many resins tend to become more ordered and compact as existing crystallites grow or new crystallites form at the expense of the more fluid parts of the amorphous material. For small additions of plasticizer, the plasticizer molecules may be totally immobilized by attachment to the resin by various forces. These tend to restrict the freedom of small portions of the polymer molecule necessary for the absorption of mechanical energy. Therefore it results in a more rigid resin with a higher tensile strength and base modulus than the base polymer itself. This phenomenon is therefore termed antiplasticization. One study used x-ray diffraction to show that small amounts of dioctyl phthalate (DOP) progressively increase the order in the PVC. Above these concentrations the order decreases and the polymer becomes plasticized.

2.6. Interaction Parameters

Early attempts to describe PVC–plasticizer compatibility were based on the same principles as used to describe solvation, ie, like dissolves like (2). To obtain a quantitative measure of PVC–plasticizer compatibility a number of different parameters have been used. More recently these methods have been assessed and extended by many workers (7–9). In all cases it is not possible to adequately predict the behavior of polymeric plasticizers.

2.6.1. The Hildebrand Solubility Parameter

This parameter, d , can be estimated (10) based on data for a set of additive constants, F , for the more common groups in organic molecules to account for the observed magnitude of the solubility parameter: $d = \Sigma F/V$ where V represents molar volume. Solubility parameters can be used to classify plasticizers of a given family in terms of their compatibility with PVC, but they are of limited use for comparing plasticizers of different families, eg, phthalates with adipates.

2.6.2. Polarity Parameter

Despite their apparent simplicity, these parameters, ϕ , show a good correlation with plasticizer activity for nonpolymeric plasticizers (10). The parameter is defined as $\phi = [M(A_p/P_0)]/1000$ where M = molar mass of plasticizer, A_p = number of carbon atoms in the plasticizer excluding aromatic and carboxylic acid carbon atoms, and P_0 = number of polar (eg, carbonyl) groups present. The 1000 factor is used to produce values of convenient magnitude. Polarity parameters provide useful predictions of the activity of monomeric plasticizers, but are not able to compare activity of plasticizers from different families.

2.6.3. The Solid–Gel Transition Temperature

This temperature, T_m , is a measure of plasticizer activity and is the temperature at which a single grain of PVC dissolves in excess plasticizer. The more efficient plasticizers show lower values of T_m as a result of their higher solvating power. This can be correlated with the ease of processing of a given plasticizer, but all measurements should be conducted with a control PVC resin since clearly the choice of resin has an effect here also.

2.6.4. The Flory-Huggins Interaction Parameter

These ideas, based on a study of polymer miscibility, have been applied to plasticizers according to the following equation in which V_1 is the molar volume of the plasticizer, obtained from molar mass figures and density values at T_m , and χ represents the interaction parameter (11).

$$1/T_m = 0.002226 + 0.1351(1 - \chi)/V_1$$

2.6.5. The Activity Parameter

Another measure (α) of plasticizer activity that is an extension of and based on earlier work gives an indication of the ease of processing for a given plasticizer with a given resin, but does not give estimates of plasticizing performance in the final product (12). M and χ are as previously defined.

$$\alpha = 1000 \frac{(1 - \chi)}{M}$$

2.7. Specific Interactions

Ideas on the subject of specific interactions between PVC and a plasticizer molecule, as a basis of plasticization, can be considered a more detailed form of some of the ideas already discussed. Clearly some mechanism of attraction and interaction between PVC and plasticizer must exist for the plasticizer to be retained in the polymer after processing.

The role of specific interactions in the plasticization of PVC has been proposed from work on specific interactions of esters in solvents (eg, hydrogenated chlorocarbons) (13), work on blends of polyesters with PVC (14–19), and work on plasticized PVC itself (20–23). Modes of interaction between the carbonyl functionality of the plasticizer ester or polyester were proposed, mostly on the basis of results from Fourier transform infrared spectroscopy (ftir). Shifts in the absorption frequency of the carbonyl group of the plasticizer ester to lower wave number, indicative of a reduction in polarity (ie, some interaction between this functionality and the polymer) have been reported (20–22). Work performed with dibutyl phthalate (22) suggests an optimum concentration at which such interactions are maximized. Spectral shifts are in the range 3–8 cm^{-1} . Similar shifts have also been reported in blends of PVC with polyesters (14–20), again showing a concentration dependence of the shift to lower wave number of the ester carbonyl absorption frequency.

These ideas have been extended using new analytical techniques, in particular molecular modeling and solid-state nuclear magnetic resonance (nmr) spectroscopy.

2.7.1. Molecular Modeling

The computer modeling of molecules is a rapidly growing branch of chemistry (24–26). High resolution graphics and fast computers allow the operator to build molecules in minimum energy configurations and view them in real time. This model can be constructed from crystallographic coordinates available from databases (qv) or by simple intervention from the operator. Molecular mechanics or quantum mechanics programs are then used to arrive at a likely structure.

A range of plasticizer molecule models and a model for PVC have been generated and energy minimized to observe their most stable conformations. Such models highlight the free volume increase caused by the mobility of the plasticizer alkyl chains. More detailed models have also been produced to concentrate on the polar region of the plasticizer and its possible mode of interaction with the polymer. These show the expected repulsion between areas on the polymer and plasticizer of like charge as well as attraction between the negative portions of the plasticizer and positive portions of the PVC.

2.7.2. Solid-State Nuclear Magnetic Resonance Spectroscopy

Advances in technology have made the study of solids by nmr techniques of considerably greater ease than in previous years. For the accumulation of solid-state ^{13}C -nmr spectra, cross-polarization magic angle spinning (CPMAS) can be utilized to significantly reduce signal broadening effects present in solid state but not in the liquid state. The technique has been used to study the molecular effects of plasticization by comparing spectral shifts of PVC and plasticizer under various degrees of processing (9, 27). For PVC plasticized with DIDP two different processing temperatures, 130 and 170°C were used, representing a low and high degree of plasticization, respectively. The comparison of the spectra showed no shift in the resonance frequency of the carbonyl group with processing temperature. The most significant difference in the two spectra was in the aliphatic carbon resonances. The spectra of the more plasticized sample showed resonance shifts and increased resolution of these carbon atoms. This again shows a strong dependence of successful plasticization on the conformation of the alkyl chains of the plasticizer ester (linked to the increased free volume).

It can be concluded from these theories and studies that plasticizer polarity is important in determining the gelation rate of the plasticizer but it does not explain other properties of interest in the final product. The conformation adopted by plasticizer molecules in the polymer matrix in the final product is clearly important because this determines how many PVC–PVC chain–chain interactions are screened from each other and how much free volume is created. The more recent studies have shown that although this conformation is important it is perhaps not so important in samples that have experienced high processing temperatures, since in these samples the separation of the PVC chains, and ingress of plasticizer, is controlled more by thermal energy than by plasticizer polarity. At lower processing temperatures the polarity of the plasticizer has a greater role in the attainment of acceptable physical properties of the final product.

3. Plasticized Polymers: The Dominance of PVC

Well over 90% of plasticizer sales by volume are into the PVC industry. The reason for such a concentration of sales is that the benefits imparted by the plasticization of PVC are far greater than those imparted to other polymers. PVC stands alone among polymers in its ability both to accept and retain large concentrations of plasticizer. This is due in part to a morphological form comprising highly amorphous, semicrystalline, and highly crystalline regions. Without the wide range of additives available, eg, plasticizers, stabilizers, fillers, lubricants, and pigments, PVC would be of little use. The development of PVC as a commodity polymer is fundamentally linked to the development of its additives.

Different types of PVC exist on the market. The two principle types are suspension and paste-forming PVC; the latter includes the majority of emulsion PVC polymers. The plasticizer applications technologies associated with these two forms are distinctly different and are discussed separately. Details of the polymerization techniques giving rise to these two distinct polymer types can be found in many review articles (5, 28) (see Vinyl polymers, (vinyl chloride polymers)).

3.1. Applications Technology

3.1.1. Suspension PVC

These polymers are produced by suspending vinyl chloride in water and polymerizing this monomer using a monomer-soluble initiator. PVC polymers produced via a suspension polymerization route have a relatively large particle size (typically 100–150 μm). Additionally, suspension polymers produced for the flexible sector have particles that are highly porous and are therefore able to absorb large amounts of liquid plasticizer during a formulation mixing cycle. A typical flexible PVC formulation (Table 2) using a suspension polymer is typically processed by a dry-blend cycle, during which all formulation ingredients are heated (typically 70–110°C) and

Table 2. Typical Flexible PVC

Ingredient	Parts by weight	Parts per hundred resin (phr)	% By weight
PVC	75	100	50
plasticizer	45	60	30
filler	26.25	35	17.5
stabilizer	3	4	2
lubricant	0.75	1	0.5
<i>Total</i>	<i>150</i>	<i>200</i>	<i>100</i>

intimately mixed to form a dry powder (the PVC dry blend or powder blend), ie, a powder that contains all formulation ingredients. This dry blend can be either stored or processed immediately. Processing of suspension resin formulations is performed by a variety of techniques such as extrusion, injection molding, and calendering to totally fuse the formulation ingredients and therefore produce the desired product.

The dry blend can also be extruded and the extrudate chipped to produce pellets of PVC compound which can then be subsequently reprocessed to produce the final product. This has the benefit of ease of storage of raw materials since all the formulation ingredients are contained bound in the gelled compound. Many producers of flexible PVC only purchase PVC compound, and many companies exist solely to produce PVC compound rather than a true end product such as sheet, flooring, or pipe.

3.1.2. Paste-Forming Polymers

Paste- or plastisol-forming PVC polymers differ from their suspension analogues in that after mixing with plasticizer they produce a paste or plastisol, similar in appearance to paint, rather than a dry blend. In this respect these polymers are used for flexible applications only. The plastisol can then be spread, coated, rotationally cast, or sprayed for processing. Plastisol-forming polymers are produced by microsuspension polymerization or emulsion polymerization. Microsuspension produces very fine particles of monomer to ensure small particle sizes of polymer are produced. In emulsion polymerization the vinyl chloride is polymerized using a water-soluble initiator; the vinyl chloride particles are small and stabilized using surfactants. There are also several variations of these two basic techniques.

Much lower particle size resins are produced by these routes, relative to suspension resins, but they also differ in that some residual surfactant from the polymerization process is retained on the polymer. The low particle size imparts a lack of porosity to the resin and thus the mixing of formulation ingredients using a dry-blending cycle is not possible. The demands on plasticizer behavior in a plastisol tends to be more complex than that in suspension technology since choice of plasticizer is made with consideration given to the required viscosity of the plastisol and also the required rheology of the plastisol. Each paste-forming polymer shows individual characteristics with respect to particle size and particle size distribution, and therefore plastisol viscosity and rheology, and no two polymers behave the same way, thus making the choice of plasticizer for this sector somewhat complex. All plasticizer types find use in this area, the choice being governed by a compromise of properties. Even polymeric plasticizers, with their very high inherent viscosities, can find use if their addition level is very high, and it is certainly common to encounter formulations with two or three different plasticizers present.

Plastisols may also be semi-gelled for storage, ie, enough heat is imparted to convert the plastisol into a solid but without the full development of tensile properties brought about by full fusion.

Because the formulation ingredients in a plastisol are in liquid form, viscosity of the plastisol is of great importance and the intrinsic viscosity of the plasticizer contributes significantly to the plastisol viscosity, as does the precise polymerization conditions of the resin. The desired plastisol viscosity can be obtained by careful selection of polymer, plasticizer, and other formulation ingredients, but the shear rate applied to the plastisol

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also affects the viscosity. PVC plastisols are either (1) pseudoplastic or shear-thinning, ie, viscosity decreases with shear; (2) near-Newtonian, ie, viscosity remains nearly constant with shear; or (3) dilatant, ie, viscosity increases with shear. Example applications exist where each of these three rheological behaviors are preferred, and precise knowledge of how a given plasticizer acts with a given resin is often required.

3.2. Effect of Plasticizer Choice on the Properties of Flexible PVC

A change in plasticizer affects the properties of a flexible PVC article. Certain properties are more important for some applications than others and hence some plasticizers find more extensive use in some application areas than others. The PVC technologist must ascertain the most important properties for an application and then make the correct choice of plasticizer.

3.2.1. Plasticizer Efficiency

This is a measure of the concentration of plasticizer required to impart a specified softness to PVC. Such a softness of material may be measured as a British Standard Softness (BSS) or a Shore hardness (Fig. 1). For a given acid constituent of plasticizer ester, ie, phthalate, adipate, etc, plasticizer efficiency decreases as the carbon number of the alcohol chain increases, eg, for phthalate esters efficiency decreases in the order DBP > DIHP > DOP > DINP > DIDP > DTDP. An additional six parts per hundred in PVC of DIDP rather than DOP is required to give a hardness of Shore 80 when all other formulation ingredients remain constant. The consequence of this depends on the overall formulation and product costs. In addition to size of the carbon number of the alcohol chain, the amount of branching is also significant; the more linear isomers are of greater efficiency. Choice of the acid constituent can also be significant. For equivalent alcohol constituents, phthalate and adipate esters are approximately equivalent but both are considerably more efficient than the trimellitate equivalent.

Reasons for these trends are clearly related to the polarity of the plasticizer and its ability to impart free volume by chain separation. Differences in polarity affect the temperature at which the plasticizer can penetrate the polymer matrix and the magnitude of the interaction with the polymer chain that results.

3.2.2. High Temperature Performance

High temperature performance in flexible PVC and its production are related to plasticizer volatilization and plasticizer degradation (Fig. 2). Plasticizer volatilization, both from the finished article during use at elevated temperatures, eg, in electrical cable insulation, and also during processing, ie, release of plasticizer fume is directly related to the volatility of the plasticizer in use. Hence the higher molecular weight plasticizers give superior performance in this area. For phthalate plasticizers, thermal stability decreases in the order DTDP > DIDP > DINP > DOP > DIHP > DBP. Higher molecular weight esters such as trimellitates are even more thermally stable and trimellitate esters find extensive use in the demanding cable specifications which have strict mass loss requirements.

Polyester plasticizers give the best performance in this area, with performance increasing with molecular weight. Additionally, branched esters have somewhat higher volatilities than their linear equivalents.

For the generation of fume in the workplace, the same structure relationships apply. Not only does excessive plasticizer volatilization have environmental consequences, but inaccuracies on formulation can be incurred since not all the plasticizer in use is entering the PVC resin, resulting in a harder material than calculated. Estimates have been made of the exact amount of plasticizer loss to the environment (29). As a result of environmental protection legislation, more end users are looking to means of recovering and re-using plasticizer fume and breakdown products, either through re-use in the processing operation or as an alternative fuel.

Plasticizer molecules can undergo thermal degradation at high temperatures. Esters based on the more branched alcohol isomers are more susceptible to such degradation. This can, however, be offset by the

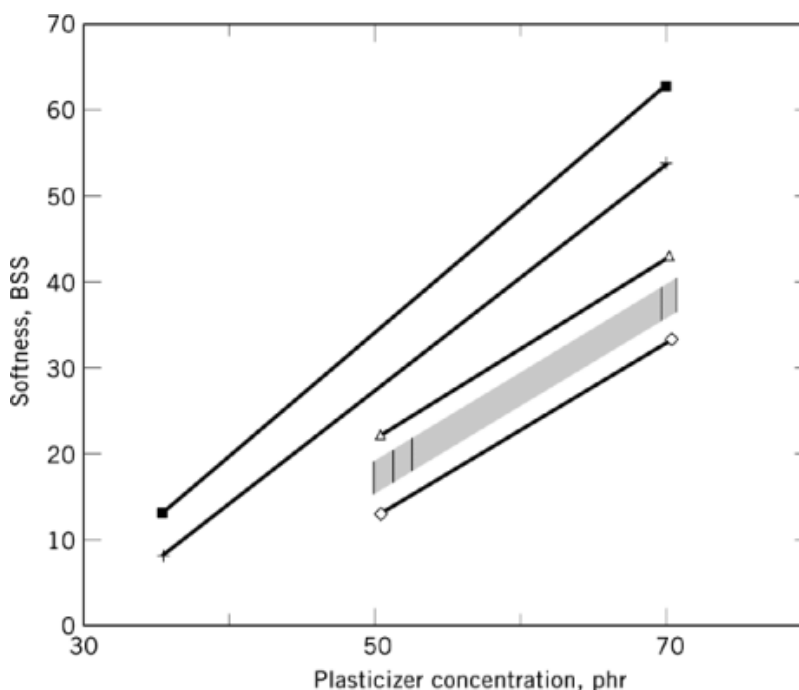


Fig. 1. Relative efficiency of plasticizers where ■ represents C₈ phthalate; +, C₁₀ phthalate; △, C₁₁ phthalate; and ◇, C₁₃ phthalate; phr=parts per hundred rubber. Values for the trimellitates fall in the shaded area. BSS 35 is equivalent to a Shore A hardness of 80, test method BS2782.

incorporation of an antioxidant, and plasticizer esters for cable applications frequently contain a small amount of an antioxidant such as bisphenol A.

3.2.3. Low Temperature Performance

The ability of plasticized PVC to remain flexible at low temperatures is of great importance in certain applications, eg, external tarpaulins or underground cables. For this property the choice of the acid constituent of the plasticizer ester is also important. The linear aliphatic adipic, sebacic, and azelaic acids give excellent low temperature flexibility compared to the corresponding phthalates and trimellitates (Fig. 3).

There is also a significant contribution to low temperature performance from the alcohol portion of the ester; the greater the linearity of the plasticizer the greater the low temperature flexibility. It might be concluded that the best low temperature plasticizer would be one based on a long and linear dibasic acid with long, straight-chain alcohols. Although this is true, other requirements must be taken into account, and it is likely that such a material would have low plasticizing efficiency, poor gelation properties, and be of limited compatibility.

3.2.4. Gelation Properties

The gelation characteristics of a plasticizer are related to its efficiency and both properties are often discussed together. The gelation characteristics are a measure of the ability of a plasticizer to fuse with the polymer so as to set up a product of maximum elongation and softness, ie, maximum plasticization properties (Fig. 4). Gelation properties are often measured either as a processing temperature, the temperature to which the plasticizer and polymer must be heated in order to obtain these properties, or as a solution temperature, the

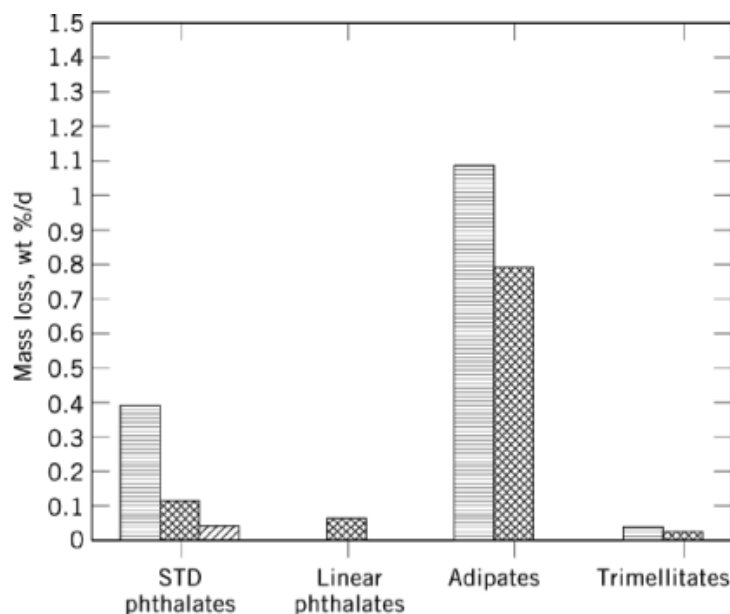


Fig. 2. Volatile loss of plasticizers from flexible PVC (BSS 35) where \square represents C₈; \boxtimes , C₁₀; and \blacksquare , C₁₃. Weight loss per day is at 100°C.

temperature at which one grain of polymer dissolves in excess plasticizer, giving a measure of the solvating power of the plasticizer. Ease of gelation is related to plasticizer polarity and molecular size. The greater the polarity of a plasticizer molecule the greater the attraction it has for the PVC polymer chain and the less additional energy, in the form of heat, is required to cause maximum plasticizer–PVC interactions. The most active plasticizers are able to bring about these effects soon after the T_g of the polymer (70–80°C) is reached, whereas the less active plasticizers require temperatures on the order of 180°C in order for the maximum elongation properties to be obtained. The polarity of the plasticizer is determined by both acid type and alcohol chain length. Aromatic acids, being of greater polarity, tend to show greater ease of gelation than aliphatic acid-based esters. Molecular size also has a key contribution and explains why molecules of similar polarity can show different gelation properties. The smaller the plasticizer molecule the easier it is for it to enter the PVC matrix; larger molecules require more thermal energy to establish the desired interaction with the polymer. Because branching influences molecular size, this too has a contribution to gelation properties, with the more branched isomers showing greater activity. Thus for the phthalate esters ease of gelation rate decreases in the order BBP > DBP > DIHP > DOP > DINP > IDP > DTDP.

3.2.5. Migration and Extraction

When plasticized PVC comes into contact with other materials, plasticizer may migrate from the plasticized PVC into the other material. The rate of migration depends not only on the plasticizer employed but also on the nature of the contact material.

Plasticizer can also be extracted from PVC by a range of solvents including water. The aggressiveness of a particular solvent depends on its molecular size and its compatibility with both the plasticizer and PVC. Water extracts plasticizer very slowly, oils are slightly more aggressive, and low molecular weight solvents are the most aggressive.

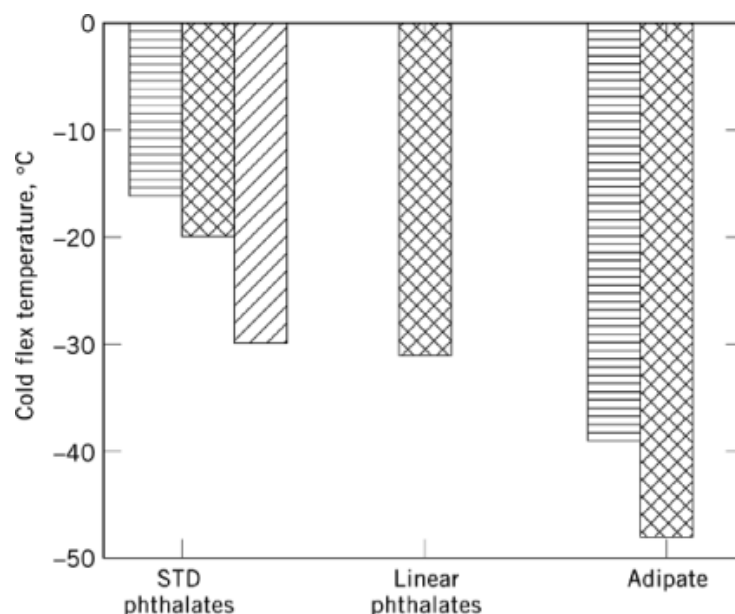


Fig. 3. Low temperature performance of plasticizers in flexible PVC (BSS 35) where \equiv represents C₈; \boxtimes , C₁₀; and \diagup , C₁₃.

The key characteristic for migration and extraction resistance is molecular size. The larger the plasticizer the less it tends to migrate or be extracted. The extreme case is seen by the use of polymeric plasticizers in applications where excellent migration and extraction resistance is required, and food packaging film applications present a relatively large market for these specialty plasticizers. There is also a contribution from the linearity of the alcohol component of the plasticizer ester. The greater the linearity of the ester the greater its migration and extraction rate in comparison to the more branched isomers.

3.2.6. *Plastisol Viscosity and Viscosity Stability*

After the primary contribution of the resin type in terms of its particle size and particle size distribution, for a given PVC resin, plastisol viscosity has a secondary dependence on plasticizer viscosity. The lower molecular weight and more linear esters have the lowest viscosity and hence show the lowest plastisol viscosity, ie, plastisol viscosity for a common set of other formulation ingredients increases in the sequence DBP < DIHP < DOP < DINP < DIDP. In spite of these viscosity differences, however, if plastisols are being formulated to equal softness, ie, taking into account the efficiency of the plasticizers involved, more of the less efficient plasticizer has to be employed in the plastisol so as to impart the same softness to the product being manufactured. The addition of this extra liquid to the plastisol may produce an equivalent viscosity to that of the plastisol with the less viscous plasticizer. Esters based on aliphatic acids, being of lower viscosity than the corresponding aromatic acids, show lower plastisol viscosities. Adipate esters have found widespread use in plastisol applications although due to other requirements, eg, volatility, gelation characteristics, etc, they are often employed in a blend with other esters.

Plastisols are often mixed and then stored rather than processed immediately (Fig. 5). It is of great importance in this case for the plasticizer to show little or no paste thickening action at the storage temperature, and clearly it is not advisable to use a plasticizer of too great an activity, since grain swelling, leading to plastisol viscosity increase, can occur at low temperatures for some active plasticizer systems.

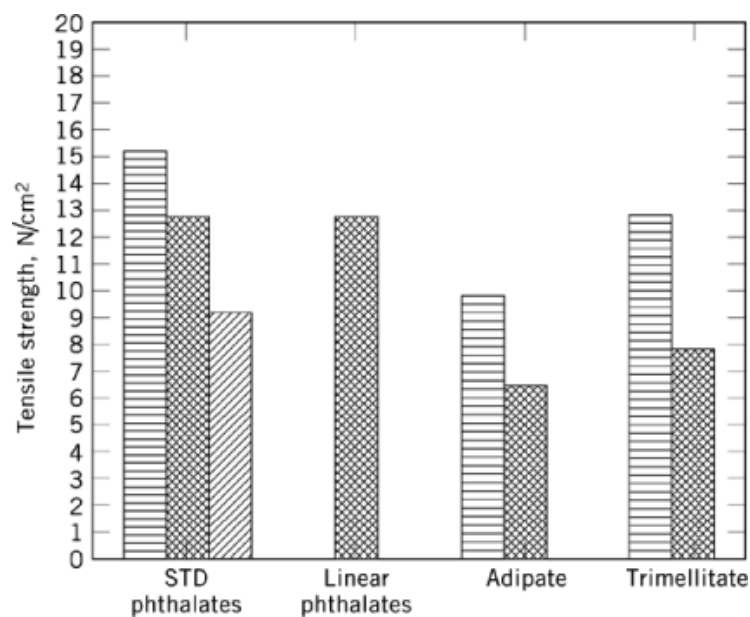


Fig. 4. Tensile strength of various PVC-plasticizer combinations when fused at 160°C where ▨ represents C₈; ▩, C₁₀; and ▤, C₁₃. To convert N/cm² to MPa, divide by 100; to convert to psi, multiply by 1.45.

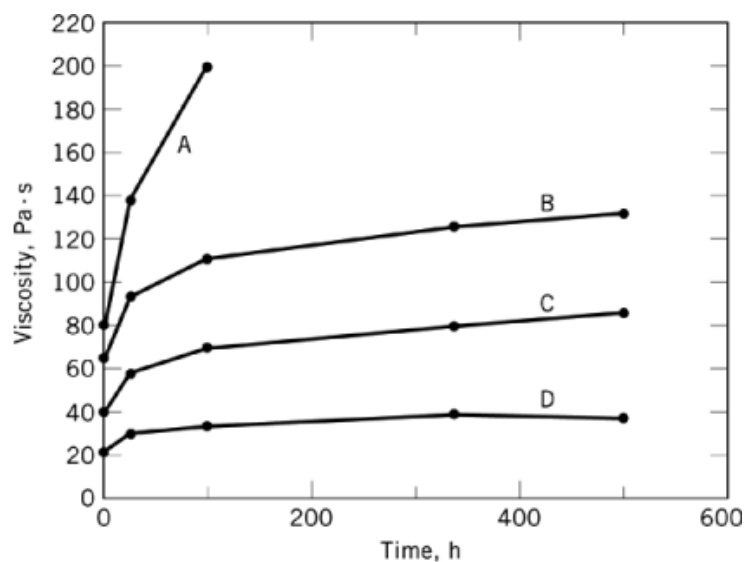


Fig. 5. Viscosity aging of plastisols at 23°C where A is BBP/DIPB; B, DOP; C, F110; and D, 911P.

3.2.7. Automotive Windshield Fogging

The phenomenon of car windshield fogging has been known for some time. The term fogging relates to the condensation of volatile material on the car windshield causing a decrease in visibility. Although this volatile material may arise from a variety of sources, eg, exhaust fume being sucked in through the ventilation system,

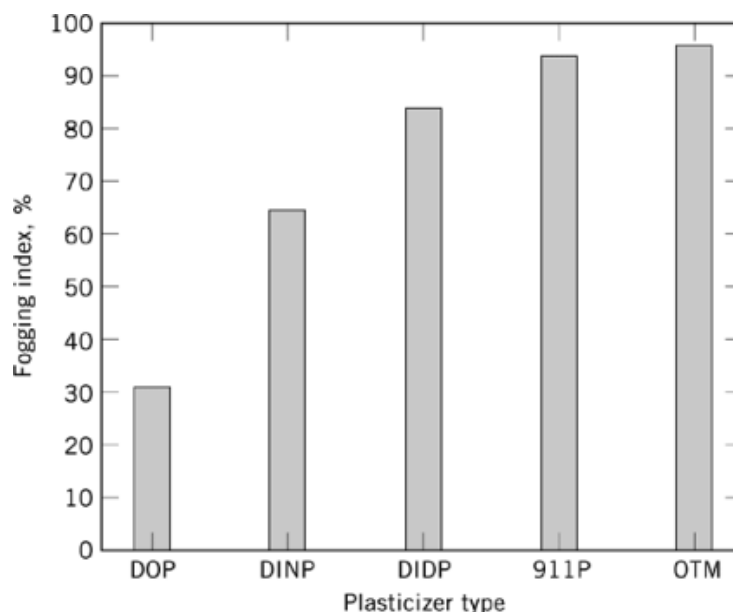


Fig. 6. Fogging index of various plasticizers for 6 at 90°C.

material from inside the car, eg, crash pads or rear shelves, may also contribute to windscreen fogging on account of the high temperatures that can be encountered inside a car when standing in sunlight. In the case of flexible PVC such a contribution may arise from emulsifiers in the polymer, stabilizers, and plasticizers.

In each case manufacturers have studied their products in detail and recommend low fogging polymers, stabilizers, and plasticizers. Tests have been designed (eg, DIN 75 201) to assess the fogging performance of both the PVC sheet and the raw materials used in its production (Fig. 6). These tests involve heating of the sheet of raw material for a specified period at a set temperature in an enclosed apparatus with a cooled glass plate above the sheet or raw material. The reflectance of the glass plate is then compared before and after the test to ascertain the degree of fogging. In such a test, the fogging performance of a plasticizer is related to its volatility, refractive index, and surface tension. The precise nature of refractive index and surface tension is somewhat complex (30) and attempts to improve the test are in progress (31). In the case of plasticizer volatility it is clear that a higher concentration of plasticizer leads to increased fogging in the test. The higher molecular weight and more linear plasticizers give superior performance. Trimellitate esters and 9,11-phthalates, with their high degree of linearity and consequently low viscosity for plastisol applications, have achieved widespread use as low fogging plasticizers for these applications.

3.2.8. Overall Assessment of Properties

Table 3 shows the effect for each criterion of increasing plasticizer concentration, increasing the size of the plasticizer molecule, increasing the linearity of the plasticizer molecule, and changing the acid constituent of the ester. An I indicates improved performance for a particular property, a P indicates poorer performance. I and P in parentheses indicate that any changes tend to be marginal.

There is clearly no perfect plasticizer for every application. Choice depends on the performance requirements of the article being manufactured and price.

Table 3. Structure:Property Relationships of Plasticizer^a

Property, at equal softness	Increased concentration	Increase size	Increased linearity	Acid ^b
efficiency, higher temperature		P	I	Ph = Ad > Tr
high	P	I	I	Tr > Ph > Ad
low	I	I	I	Ad > Ph = Tr
gelation	(I)	P	(P)	Ph > Ad ≥ Tr
migration/extraction	P	I	P	Tr > Ph > Ad
plastisol				
viscosity	I	(I)	I	Ad > Ph
aging		I	(I)	Ad > Ph
fogging	P	I	I	Tr > Ph > Ad

^a I = improved performance; P = poorer performance; (), marginal performance.

^b Ph = phthalate; Ad = adipate; Tr = trimellitate.

4. The Plasticization of Polymers Other Than PVC

The plasticization of PVC accounts for the vast majority of plasticizer sales. However, significant amounts of plasticizers are used in non-PVC polymers and this may become increasingly important in the future. Although PVC stands alone in its ability to accept and retain large quantities of commercial plasticizer, effective plasticization of other resins using slightly modified plasticizers may be possible if certain conditions specific to the polymer of interest are met.

The first factor to be considered when looking at the plasticization of a polymer is the need; even though some polymers may be compatible with large concentrations of plasticizer, the resultant softening benefits may be of little use. Other factors are short- and long-term compatibility, ie, the ability of a polymer to accept and retain the plasticizer.

In order for a plasticizer to enter a polymer structure the polymer should be highly amorphous. Crystalline nylon retains only a small quantity of plasticizer if it retains its crystallinity. Once it has penetrated the polymer the plasticizer fills free volume and provides polymer chain lubrication, increasing rotation and movement.

The plasticizer content of a polymer may be increased by the suppression of crystallization in the polymer, but if crystallization subsequently occurs the plasticizer exudes. For highly crystalline resins, the small amounts of plasticizer allowable can change the nature of the small amorphous regions with a consequent overall change in properties.

4.1. Acrylic Polymers

Although considerable information on the plasticization of acrylic resins is scattered throughout journal and patent literature, the subject is complicated by the fact that acrylic resins constitute a large family of polymers rather than a single polymeric species. An infinite variation in physical properties may be obtained through copolymerization of two or more acrylic monomers selected from the available esters of acrylic and methacrylic acid (30) (see Acrylic ester polymers; Methacrylic acid and derivatives).

Plasticizers, however, are used in the acrylics industry to produce tough, flexible coatings. Compatibilities with common plasticizers are up to 10 wt % although in some cases, for low molecular weight plasticizers, it can be higher. For example, a formulation of 100 phr PMMA, 150 phr DBP, 225 phr chalk, and 25 phr resorcinol has been used (6). PMMA is used in small amounts with PVC. Cast acrylics, however, require a high T_g and high rigidity, hence no plasticizer application is required.

Plasticizers for acrylics include all common phthalates and adipates. There has been interest in the development of acrylic plastisols similar to those encountered with PVC. Clearly the same aspects of both plastisol viscosity and viscosity stability are important. Patents appear in the literature (32) indicating that the number of available plasticizers that show both good compatibility with acrylic resins and satisfactory long-term plastisol stability may be fewer than those showing equivalent properties with emulsion PVC resins.

Patents have appeared (33, 34) which show formulations containing PMMA emulsion polymer and PMMA suspension polymer combined with benzyl butyl phthalate and octyl benzyl phthalate. It is likely that polymers of this type will require highly polar plasticizers in order to have both adequate compatibility and adequate gelation. When replacing PVC applications the use of large quantities of phosphate plasticizers is sometimes required to give equivalent fire performance.

4.2. Nylon

The high degree of crystallinity in nylon means that plasticization can occur only at very low levels. Plasticizers are used in nylon but are usually sulfonamide based since these are generally more compatible than phthalates. DEHP is 25 phr compatible; other phthalates less so. Sulfonamides are compatible up to 50 phr.

4.3. Poly(ethylene terephthalate)

PET is a crystalline material and hence difficult to plasticize. Additionally, since PET is used as a high strength film and textile fiber, plasticization is not usually required although esters showing plasticizing properties with PVC may be used in small amounts as processing aids and external lubricants. Plasticizers have also been used to aid the injection molding of PET, but only at low concentrations.

The main area of interest for plasticizers in PET is in the area of dyeing. Due to its lack of hydrogen bonds PET is relatively difficult to dye. Plasticizers used in this process can increase the speed and intensity of the dyeing process. The compounds used, however, tend to be of low molecular weight since high volatility is required to enable rapid removal of plasticizer from the product (see Dye carriers).

4.4. Polyolefins

Interest has been shown in the plasticization of polyolefins (5) but plasticizer use generally results in a reduction of physical properties (12), and compatibility can be achieved only up to 2 wt %. Most polyolefins give adequate physical properties without plasticization. There has been use of plasticizers with polypropylene to improve its elongation at break (7) although the addition of plasticizer can lower T_g , room temperature strength, and flow temperature. This can be overcome by simultaneous plasticization (ca 15 wt % level) and cross-linking. Plasticizers used include DOA.

4.5. Polystyrene

Polystyrene shows compatibility with common plasticizers but modification of properties produced is of little value. Small amounts of plasticizer (eg, DBP) are used as a processing aid.

4.6. Fluoroplastics

Conventional plasticizers are used as processing aids for fluoroplastics up to a level of 25% plasticizer. However, certain grades of Kel-F (chlorotrifluoroethylene) contain up to 25 wt % plasticizer to improve elongation and increase softness; the plasticizers used are usually low molecular weight oily chloroethylene polymers (5).

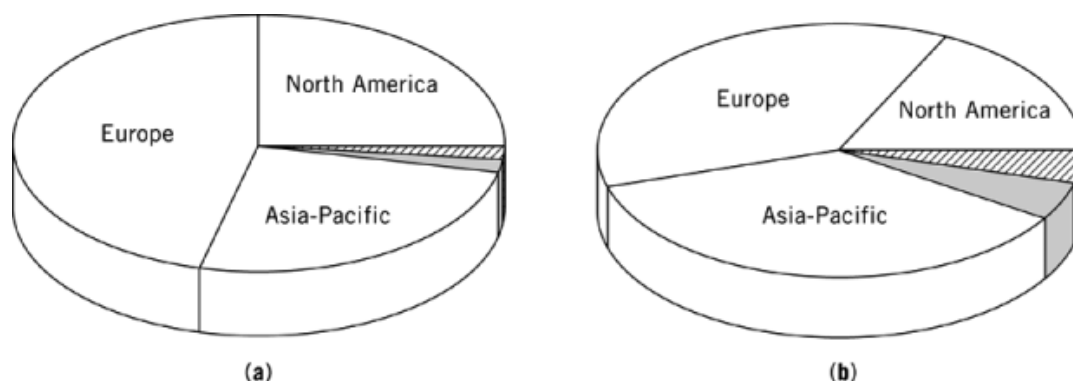


Fig. 7. Worldwide plasticizer production (a) and consumption (b) where▨ represents Africa and the Near East and ■, Latin America (31).

4.7. Rubbers

Plasticizers have been used in rubber processing and formulations for many years (8), although phthalic and adipic esters have found little use since cheaper alternatives, eg, heavy petroleum oils, coal tars, and other predominantly hydrocarbon products, are available for many types of rubber. Esters, eg, DOA, DOP, and DOS, can be used with latex rubber to produce large reductions in T_g . It has been noted (9) that the more polar elastomers such as nitrile rubber and chloroprene are insufficiently compatible with hydrocarbons and require a more specialized type of plasticizer, eg, a phthalate or adipate ester. Approximately 50% of nitrile rubber used in Western Europe is plasticized at 10–15 phr (a total of 5000–6000 t/yr), and 25% of chloroprene at ca 10 phr (ca 2000 t/yr) is plasticized. Usage in other elastomers is very low although may increase due to toxicological concerns over polynuclear aromatic compounds (9).

Studies on the use of high molecular weight esters in nitrile rubber have led to further studies to compare DINP with DBP. These showed that at the 10 phr level the nitrile rubber was effectively plasticized with DINP (35).

5. Economic Aspects

Worldwide consumption of plasticizers is estimated at 3.5×10^6 t (31), and is of the order of 1 million tons in Western Europe (Fig. 7; Table 4). The distribution of plasticizers into various applications is as follows: 27%, wire and cable covering; 23%, extrusion/profile; 17%, film and sheet; 13%, coated fabrics; 12%, wall covering; and 8%, undersealing/coating.

6. Health and Safety Aspects

Numerous toxicological studies have been conducted on a variety of plasticizers. However, because di-(2-ethylhexyl) phthalate (DEHP) is the most widely used plasticizer and is a well-defined single substance, it is the plasticizer that has been most thoroughly investigated in terms of its toxicology and has often been considered as a model for the other phthalates (36).

Table 4. Western European Plasticizer Market^a

Plasticizer	Market share, %
<i>Overall market</i>	
C ₈ phthalates	47
C ₉ and C ₁₀ phthalates	32
C ₄ phthalates	6
C ₇ and C ₁₁ phthalates	2
linear phthalates	1
other specialties	12
<i>Specialty market</i>	
epoxies ^b	20
adipates	14
phosphates	13
BBP	12
sulfonates	11
polymeric	10
linear phthalates	10
trimellitates	7
DTDP	2
azelates/sebacates	1

^aApproximate split by grade types.^bESBO, etc.

6.1. Acute Toxicity

Plasticizers possess an extremely low order of acute toxicity; LD₅₀ values are mostly in excess of 20,000 mg/kg body weight for oral, dermal, or intraperitoneal routes of exposure. In addition to their low acute toxicity, many years of practical use coupled with animal tests show that plasticizers do not irritate the skin or mucous membranes and do not cause sensitization.

6.2. Chronic Toxicity

The effects of repeated oral exposure to phthalates for periods ranging from a few days to 2 years have been studied in a number of animal species including rats, mice, hamsters, guinea pigs, ferrets, and dogs (37).

6.2.1. Liver Effects

In 1980 a 2-year feeding study carried out as part of the NTP/NCI Bioassay Program in the United States (38, 39) indicated that DEHP causes increased incidence of liver tumors in rats and mice and that DEHA had a similar effect in mice but not rats. In these studies the levels of plasticizers fed were very high, this being possible only because of their low acute toxicity.

A large number of more recent investigations (37) on a variety of plasticizers and different animal species have revealed the following. (1) Plasticizers are not genotoxic. (2) Oral administration of plasticizers, fats, and other chemicals including hypolipidemic drugs to rodents causes a proliferation of microbodies in the liver (peroxisomes) which may be considered to be linked to the formation of liver tumors. (3) Administration of plasticizers, fats, and hypolipidemic drugs to nonrodent species such as marmosets (40) and monkeys (41) does not lead to peroxisome proliferation and liver damage. Some hypolipidemic drugs which cause peroxisome proliferation in rodents have been used by humans for many years with no ill effects. (4) These species differences have also been observed in *in vitro* studies. Phthalates, their metabolites, and a variety of other peroxisome proliferators caused peroxisome proliferation in rat and mouse liver cells but not in those of humans, marmosets, or guinea pigs.

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On the basis of these differences in species response it was concluded that phthalates do not pose a significant health hazard to humans. This view is borne out by the EU Commission decision of July 25, 1990 which states that DEHP shall not be classified or labeled as a carcinogenic or an irritant substance (42). This has been reaffirmed in a comprehensive review (43) which concludes that “peroxisome proliferators constitute a discrete class of nongenotoxic rodent hepatocarcinogens and that the relevance of their hepatocarcinogenic effects for human hazard assessment is considered to be negligible.”

The International Agency for Research on Cancer (IARC) has classified DEHP (44) as “an agent possibly carcinogenic to humans.” However this classification is based only on the rodent studies and does not take into account the more recent understanding of the underlying mechanisms.

6.2.2. Reproductive Effects

Phthalates have been shown to cause reproductive effects in rats and mice but primates are resistant to these effects. This may be due in part to pronounced differences in the way in which phthalates are metabolized by rodents and primates, including humans.

The reproductive toxicity of some phthalate esters has been reviewed by the Commission of the European Communities (45). This review concludes that testicular atrophy is the most sensitive indicator of reproductive impairment and that the rat is the most sensitive species.

Comparing estimates of the average human daily lifetime exposure to DEHP (0.3-6 $\mu\text{g/kg}$ body weight per day) to the level at which no effects are observed in rats indicates that the margin of safety for the general public is more than 10,000. Taking into consideration the significant difference in species sensitivity between rodents and primates, the safety factor is in fact even greater.

7. The Effect of Plasticizers on the Environment

About one million tons of plasticizers are used annually in Western Europe. Some 92% of this total is used to plasticize poly(vinyl chloride) (PVC) and about 95% of these PVC plasticizers are phthalate esters. In spite of the fact that there are several hundred plasticizers in commercial use in the world, only relatively few (ie, phthalates) are used in amounts that make them significant in tonnage terms, and hence in their likely environmental input and impact.

7.1. Estimated Emissions to the Environment

Phthalates may be emitted to the environment during their incorporation into PVC and from the finished PVC article during its use or after its final disposal. However, because their purpose is to make PVC flexible and for it to remain so over long periods of time, plasticizers are of very low volatility relative to many other commonly used products, for example solvents.

The widespread usage of phthalates in flexible PVC has resulted in many investigations being made of their concentration in the environment. Unfortunately the ubiquitous presence of phthalates in laboratory chemicals and equipment has caused problems in the analysis of very low concentrations of phthalates in environmental samples and has led to erroneously high levels being reported.

The need to identify the correct environmental concentrations of phthalates was recognized by the European Council for Plasticizers and Intermediates (ECPI). In 1990 they initiated a program of work aimed at developing rational estimates of phthalate emissions together with ecotoxicological testing to determine their environmental impact. The ECPI, whose members comprise all the important manufacturers of plasticizers in Western Europe, is one of many special interest sector groups of the European Chemical Industry Council (CEFIC).

Table 5. Estimated Phthalate Emissions in Western Europe

Process/end use	Emissions, t/yr
production	220
distribution	80
processing	
calendered film and sheet	280
calendered flooring	10
spread coating	520
other plastisols	50
extrusion/injection molding	90
<i>total</i>	<i>950</i>
interior end use	
flooring	
evaporation	20
water extraction	500 ^a
wall covering	20
other film, sheet, and coating	40
wire, cable, profile, and hose	60
<i>total</i>	<i>640</i>
exterior end use	5600 ^a
disposal	250
<i>Total</i>	<i>7740</i>

^aNot well defined.

The members of ECPI are well placed to carry out this study because in addition to their intimate knowledge of plasticizer production techniques they have in-depth technical contacts with the plasticizer consuming industries and hence access to information regarding the use and fate of plasticizers. This knowledge together with the availability of accurate statistical information has enabled ECPI to develop a much more precise model of the environmental input of plasticizers than has hitherto been possible. This long program of work has resulted in the production of soundly based emission estimates (29) (Table 5) and well-designed ecotoxicological studies.

The ECPI approach has been adopted by the European Commission in their "Technical Guidance Document on the Risk Assessment of Notified New Substances" as the model for assessment of environmental exposure from additives in plastics. It is important to note, however, that due to the effect of ultraviolet degradation and microbial attack, a significant proportion of the emissions from flexible PVC consists of plasticizer degradation products. In these instances, therefore, the level of plasticizers appearing in the environment will be significantly less than indicated by the plasticizer loss data.

7.1.1. Emissions During Plasticizer Production and Distribution

Phthalate plasticizers are produced by esterification of phthalic anhydride in closed systems hence losses to atmosphere are minimal. Inquiries of all the principal plasticizer producers indicate a maximum total emission in Western Europe of 220 t/yr, 90% of which is to the water compartment. This level is expected to decrease in the future due to increasing plant water treatment.

The transport of phthalates by road tankers and ships within Europe is carried out by international companies with sophisticated tank cleaning facilities. Wash waters from these modern facilities are passed through a series of separators to remove any residual plasticizer which is then incinerated. It is estimated that, as a result of cleaning and spillages, the maximum emission to the environment is 80 t/yr.

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Table 6. Air Treatment in Flexible PVC Processing Plants in Western Europe, 1991

Treatment	Plasticizer usage, 10 ³ t/yr	Filter treated, %	Incinerated, %	Total treated, %
spread coating	192	53	22	75
slush, dip, and rotational molding	17	26	6	32
automotive underseal	67		100	100
calendered sheet and film	138	23	25	48
calendered flooring	31	15	56	81

7.1.2. Emissions During Processing

During the production of flexible PVC products plasticizers are exposed for up to several minutes to temperatures of $\sim 180^{\circ}\text{C}$. The exact conditions depend on the processing technique employed, but it is evident that the loss of plasticizer by evaporation and degradation can be significant.

Of the various processing techniques used, injection molding and extrusion involve little or no exposure of hot product to the surrounding air, hence they give rise to no significant emission of plasticizer to the atmosphere. This is not the case in the production of sheet and film by calendering or spread coating.

Air extracted from spread coating ovens contains typically 500 mg/m³ plasticizer which is present mostly as an aerosol since the saturation concentration of common plasticizers in air is low. In those installations with filtration equipment, the average phthalate concentration in the air is reduced from 500 mg/m³ to below 20 mg/m³. The use of incineration equipment to clean the exhaust air reduces the residual phthalate concentration to practically zero. The use of filters and incinerators on calendering and spread coating plants is steadily increasing due primarily to the need to reduce emissions of solvents and other volatile organic compounds. Consequently a large proportion (69% in 1990 and increasing) of all the phthalates in calendering and plastisol applications in Western Europe are used in processing plants equipped with incinerators or filters (Table 6).

Knowledge of the quantity of plasticizer used in each application together with the level of exhaust air treatment allows estimation of the level of plasticizer lost to atmosphere during these processes.

7.1.3. Emissions During Interior End Use

The majority of flexible PVC is used indoors in applications such as flooring, wall covering, upholstery, wire and cable, etc. Environ Corporation, consultants to the CMA, have developed a model (46) which attempts to quantify the plasticizer losses that occur in a typical room. Using theoretical and semiexperimental approaches they have arrived at an emission rate at 25°C of 2.3×10^{-4} mg/s/m². Using this emission rate with data on the annual production of PVC flooring, wallcovering, etc, and estimates of their lifetimes it is straightforward to calculate the plasticizer losses from all indoor flexible PVC articles.

Some products, particularly flooring, may lose plasticizer not only by evaporation but also through extraction by soapy water during cleaning. It is possible to estimate the quantity of plasticizer extracted but many assumptions have to be made including the frequency, duration, and temperature of washing and the proportion of floors cleaned in this way. Wastewater associated with the cleaning process typically goes to the municipal sewage system. Thus, the phthalates are biodegraded and do not end up in the environment.

7.1.4. Emissions During Exterior End Use

When flexible PVC is used in exterior applications plasticizer loss may occur due to a number of processes which include evaporation, microbial attack, hydrolysis, degradation, exudation, and extraction. It is not possible, due to this wide variety of contribution processes, to assess theoretically the rate of plasticizer loss by exposure outdoors. It is necessary, therefore, to carry out actual measurements over extended periods in real

life situations. Little suitable data have been published with the exception of some studies on roofing sheet (47). The data from roofing sheet has been used to estimate the plasticizer losses from all outdoor applications. This estimate may well be too high because of the extrapolation involved. Much of this extracted plasticizer does not end up in the environment because considerable degradation takes place during the extraction process.

7.1.5. Emissions During Disposal and Incineration

The increasing use of modern incinerators to dispose of domestic waste results in complete combustion of plasticizers to carbon dioxide and water. The preponderance of plasticizer going into landfills is as plasticized PVC. Once a landfill has been capped anaerobic conditions prevail and it is biologically relatively inactive. Under these conditions the main route by which organic components are removed from the landfill contents is by ingress of water, extraction, and subsequent loss of water from the site to the environment.

In the United Kingdom there are approximately 2000 active landfill sites with an annual combined water ingress of $40 \times 10^6 \text{ m}^3$ (48, 49). The solubility of the most common plasticizer, DEHP, in water is difficult to measure. The true solubility is considered to be around $50 \text{ } \mu\text{g/L}$ (50, 51), but various values are given in the literature. Assuming a worst case solubility of 1 ppm then the maximum quantity of plasticizer extracted is 40 t/yr. If the United Kingdom is typical of the whole of Europe, and assuming that waste is proportional to population, then a maximum of 250 t/yr plasticizer could be emitted to the environment from landfills in Western Europe. To obtain a more precise estimate of the situation, 25 effluent water samples from a variety of types of U.K.-based landfills have been analyzed. The highest concentration of DEHP detected was 30 parts per billion. If the highest figure is used instead of the assumed 1 ppm then the quantity from the whole of Europe becomes 7.5 t.

7.2. Occurrence of Plasticizers in the Environment

The contamination of laboratory chemicals and equipment causes problems in the analysis of very low concentrations of phthalates in environmental samples. Strenuous efforts have been made to overcome these difficulties in recent studies but the results of many earlier investigations must be treated with caution.

7.2.1. Phthalates in Air

Atmospheric levels of phthalates in general are very low. They vary, for DEHP, from nondetectable to 132 ng/m^3 (50). The latter value, measured in 1977, is the concentration found in an urban area adsorbed on airborne particulate matter and hence the biological availability is uncertain. More recent measurements (52) in both industrial and remote areas of Sweden showed DEHP concentrations varying from 0.3 to 77 ng/m^3 with a median value of 2 ng/m^3 .

Atmospheric photodegradation of DEHP and DBP has been shown to be rapid (51, 53) with half-life times of less than 2 days, hence a large proportion of phthalate emissions to the air are broken down by photodegradation.

7.2.2. Phthalates in Water

Reported levels of phthalates in natural waters are, in general, low. Concentrations found in fresh waters range from nondetectable up to $10 \text{ } \mu\text{g/L}$. Measured concentrations (54) in Swedish rivers vary from 0.3 to $3.1 \text{ } \mu\text{g/L}$. The highest values are found near industrial discharge points.

In the most recent and comprehensive study, 230 measurements from 11 sampling points along 225 km of the Rhine and adjoining rivers were made over a period of one year (1991–1992). The concentration of DEHP found varied from 0.11 to $10.3 \text{ } \mu\text{g/L}$; the latter value is unusually high as evidenced by the mean concentration of only $0.82 \text{ } \mu\text{g/L}$ (55).

Plasticizer levels in surface waters are decreasing. The Netherlands National Institute of Public Health and Environmental Protection (RIVM) states that the level of phthalates in Lake Yssel fell by 75% to 0.3 $\mu\text{g/L}$ over the period 1980–1988 (56).

7.2.3. *Phthalates in Sediments*

Phthalates are lipophilic and hence partition onto organic-rich particulate matter in water. This particulate matter on settling gives rise to sediments which contain higher levels of phthalate than the overlying water. The level of DEHP in sediment at seven points along the Rhine has been found (55) to range from 1.8 to 18.3 mg/kg dry weight. Lower levels of between 0.1 and 8.9 mg/kg dry weight have been found at 10 sampling points along the Weser. The mean concentration of DEHP in sediment in the two rivers was 5 mg/kg dry weight (dw).

By taking sections from a sediment core sample of 120 cm in depth it was found that the current phthalate level is only 15% of what it had been in 1972–1978. This is despite the fact that the total usage of plasticizers has continued to increase annually.

A thorough survey of phthalate levels in sediments has been conducted in Sweden by the Environmental Research Institute (57). Samples of sediment have been taken from 22 locations varying from isolated lakes to rivers near industrial discharge points. The concentration of DEHP in the lake and river samples varied from 0.008 to 0.79 mg/kg dry weight (dw). The only high levels were found at the discharge points from two industrial sites using phthalates. The total concentrations of all phthalates at these two discharge points were 203 mg/kg dw and 34.3 mg/kg dw. Measurements at these same points in 1983 (54) gave values of 1480 and 628 mg/kg dw, respectively. The decreasing concentrations of phthalates observed between 1983 and 1994 at these two point sources is considered to be the result of improved plant wastewater management.

7.2.4. *Wastewater Treatment Plants*

Numerous studies have shown that phthalates in wastewater systems are removed to a significant extent by treatment plants. The concentration of phthalates in both domestic and industrial wastewater was measured before and after treatment (55). The total level of phthalates in domestic effluent was reduced by treatment from 32.7 to 0.92 $\mu\text{g/L}$ and in industrial effluent from 93.6 to 1.06 $\mu\text{g/L}$. Thus between 97 and 99% of the phthalates are removed from wastewater by treatment plants.

These data together with those from wastewater treatment plants at Darmstadt, Germany; Gothenburg and Stockholm, Sweden; and Noord-Brabant, the Netherlands, show that the concentrations of DEHP, and in some cases total phthalates, entering wastewater treatment plants vary from 1 to 167 $\mu\text{g/L}$. After treatment the concentrations range from <1 to 36.8 $\mu\text{g/L}$.

7.3. Environmental Modeling

The estimated plasticizer emissions outlined earlier have been entered into the HAZCHEM model developed by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC). This enables the levels of plasticizer in the various environmental compartments to be estimated. The advantage of using environmental models in conjunction with emission estimates is that they give an overview of the concentrations present in any chosen region. This is helpful in conducting realistic environmental risk assessments.

Comparison of these environmental compartment concentrations with the actual measurements made at a variety of locations show reasonable agreement but indicate that emission estimates are rather high. It is likely that the fault lies with worst case estimates for losses from outdoor applications and the washing of PVC flooring. In addition a large proportion of the phthalates lost by these routes will not enter rivers because they will be removed by wastewater treatment plants.

7.4. Environmental Effects of Plasticizers

Measurement of the effect of phthalates on environmental species is difficult because standard test methods are not designed to deal with poorly water-soluble substances. For this reason a number of early studies are flawed and their results should be disregarded in favor of more recent investigations where these difficulties have been overcome.

7.4.1. Atmospheric Toxicity

The only known atmospheric toxicity effect of phthalates is the phytotoxicity arising from the use of DBP plasticized glazing bars in greenhouses. However, the higher phthalates such as DEHP are not phytotoxic. General atmospheric concentrations of phthalates are extremely low and it is concluded that they pose no risk to plants or animals.

7.4.2. Aquatic Toxicity

The standard tests to measure the effect of substances on the aquatic environment are designed to deal with those that are reasonably soluble in water. Unfortunately this is a disadvantage for the primary phthalates because they have a very low water solubility (ca 50 $\mu\text{g/L}$) and this can lead to erroneous test results. The most common problem is seen in toxicity tests on daphnia where the poorly water-soluble substance forms a thin film on the water surface within which the daphnia become entrapped and die. These deaths are clearly not due to the toxicity of the substance but due to unsuitable test design.

The majority of studies on the acute and chronic toxicity of phthalates to aquatic organisms show no toxic effects at concentrations 200–1000 times the water solubility. However, there are some studies indicating higher toxicity which are believed to be due to the flotation and entrapment effects outlined above.

ECPI has commissioned further aquatic toxicity studies in order to clarify the situation and meet the requirements of Commission Directive 93/21/EEC, 18th adaptation to technical progress of 67/548/EEC which regulates the classification, labeling, and packaging of substances. The studies have been designed to ensure no entrapment problems. Some of these studies, investigating the effect of phthalates on the survival and reproduction of *Daphnia magna*, have been completed and demonstrate that DEHP and the higher phthalates tested do not show acute or chronic toxicity to daphnia at 1 mg/L. These results, coupled with data from biodegradation studies, confirm that the phthalates commonly used in the plasticization of PVC do not require classification “Dangerous for the Environment.”

7.4.3. Sediment Toxicity

Because of their low solubility in water and lipophilic nature, phthalates tend to be found in sediments. Unfortunately little work has previously been carried out on the toxicity of phthalates to sediment dwelling organisms. For this reason ECPI has commissioned some sediment toxicity studies designed to measure the effect of DEHP and DIDP in a natural river sediment on the emergence of the larvae of the midge, *Chironomus riparius*.

Chironomus riparius is distributed throughout North America and Europe in a wide variety of freshwater habitats. The larvae live within the sediment and after four larval stages they pupate and rise to the surface where the adult insects emerge. This 28-day study has shown that DEHP and DIDP sediment concentrations of 100, 1,000, and 10,000 mg/kg dry weight have no adverse effect on either the time to emergence or the percentage emergence of the adults. It is therefore concluded that there was no effect of either phthalate on the survival, development, and emergence of *Chironomus riparius* at any of the sediment concentrations tested. The no observed effect concentration (NOEC) of 10,000 mg/kg dry weight is far in excess of phthalate concentrations that are found even at industrial discharge points.

7.4.4. Conclusions

The impact of plasticizers on the environment is very low and is diminishing as evidenced by analytical data showing that the levels of phthalates in surface waters and sediments are decreasing. This is despite the fact that their usage has continued to increase annually and is most likely due to improved emission controls and wastewater treatment.

8. Storage and Handling

Plasticizer esters are relatively inert, thermally stable liquids with high flash points and low volatility. Consequently they can be stored safely in mild steel storage tanks or drums for extended periods of time. Exposure to high temperatures for extended periods, as encountered in drums in hot climates, is not recommended since it may lead to a deterioration in product quality with respect to color, odor, and electrical resistance.

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