2

Plasticizer Types

George Wypych
ChemTec Laboratories, Inc., Toronto, Ontario, Canada

2.1 INTRODUCTION

Table 2.1 shows consumption of plastics additives by type.[1]

Table 2.1. Consumption of plastics additives in 1999 in the USA by type. [Data from Kattas L N, Gastrock F, The Individual Additives - Dynamics of Change. Retec 2000.]

Additive types	Consumption by volume,%	Consumption by value,%
Plasticizers	59	32
Flame retardants	12	14
Impact modifiers/processing aids	8	10
Heat stabilizers	6	12
Lubricants/mold release agents	6	6
Antioxidants	3	9
Organic peroxides	2	6
Light stabilizers	1	3
Other	3	8

Plasticizers are by far the most common additives. They are also less expensive than other additives used in the polymers processing and applications.

Table 2.2 shows consumption of plasticizers by industry.[2]

Table 2.2. Consumption of plasticizers in Europe in 1994 by industry. [Data from Menzel B, Kunststoffe, 86, 7, p. 992-996, 1996.]

Industry	Consumption, %
Technical film, tarpaulins, roofing sheet	20
Compounds (cable sheathing, cable filling compounds, wire coating, seals, profiles, tubing)	19

Table 2.2. Consumption of plasticizers in Europe in 1994 by industry. [Data from Menzel B, Kunststoffe, 86, 7, p. 992-996, 1996.]

Industry	Consumption, %
Floor coverings, wallpapers	19
Cable	9
Miscellaneous (lubricants, pressure rollers, laminated glass, sheet, medical)	7
Adhesives including glazing	6
Synthetic leather	6
Paints and printing inks	6
Packaging film	4
Tubes and profiles	3

According to the data in Table 2.2, many industries require plasticizers. The geographical distribution of plasticizers among different sectors varies (see Section 14.10), although general use of plasticizers is similar. For example, 63% of plasticizers are used by the cable industry, film production, flooring, profiles, and wall coverings in Russia,[3] which is close to 67% of plasticizers used in Europe for similar purposes. Plasticizers' use is driven by the cost/performance ratios of different raw materials in the production of finished goods. Asia/Pacific is the largest market for additives (39% by mass in 1997), followed by Europe (26%) and North America (23%) with other regions using remaining 12%.[4]

Polyvinylchloride uses 80% of all plasticizers in Europe. Phthalates constitute 92% of all plasticizers used in Europe.[5] The largest production among phthalates belongs to di-(2-ethylhexyl) phthalate (51%), diisodecyl phthalate (21%), and diisononyl phthalate (11%). This varies from country to country. In Russia, which manufactures 300,000 tons of plasticizers (Europe manufactures over 1,300,000 tons of various plasticizers),[5-7] di-(2-ethylhexyl) phthalate constitutes 65.1% of total production and the total phthalates constitute 98% of all plasticizers.[3] The use of plasticizers changes recently because of reported findings and regulations (see Chapters 18-21). Phthalates and some chloroparaffins are the most affected groups. Production of phthalic anhydride, which is principally used for production of phthalic esters, slightly decreases.[8] This may signalize that further changes in the produced types of plasticizers are to be expected. Implication of plasticizers in health and safety issues caused some market analysts and manufacturers to report additives growth with the exclusion of plasticizers[9] to display a higher growth. The plasticizers' growth until 2006 is expected to be 2.7%, which is at about an average of additives' growth.[6] There are various speculations regarding potential replacements for phthalates but these predictions may be far from future realities because various research studies still produce many conflicting results. The broad knowledge base gives the best chances for the proper decision-making process.

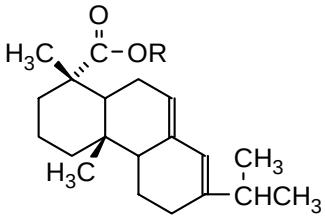
In the next section, plasticizers are discussed in twenty-four sections. Twenty-two sections are based on chemical similarity and two are based on applications (explosives and cementitious products) because chemical compositions of these plasticizers are very different than the plasticizers used in other markets.

The discussion in the next section is designed to find common features of plasticizers within the same chemical group and to provide information that is suitable for comparison of properties of plasticizers from different chemical groups. This section does not contain information on specific plasticizers. Information on specific plasticizers is included in a special electronic publication on CD-ROM.[10] The CD-ROM database contains specific data on over 1200 commercial plasticizers as supplied by manufacturers as well as a large number of data on chemical compounds which are the components of plasticizers.[10] Both publications – the book and the database – were designed and prepared to complement each other in providing information based on a broad collection of data available worldwide.

2.2 CHARACTERISTIC PROPERTIES OF INDUSTRIAL PLASTICIZERS

2.2.1 ABIETATES

Technical abietic acid is obtained by heating rosin with or without acids. The following is the chemical formula of abietic acid esters:

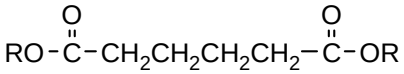


$R = CH_3$ or CH_2CH_3

Only methyl and ethyl esters are produced on a commercial scale. Use is rapidly declining because both rosin and esters of abietic acid are known allergens. Abietates have high boiling points (methyl abietate – 360°C). Rosin and abietates are considered to be plasticizers and tackifiers. Potentially they may be used in caulks, adhesives, and varnishes.

2.2.2 ADIPATES

The esters of adipic acid have the following chemical structure:



The following table contains comparative data for this group of plasticizers. Similar to other groups, minimum and maximum values are usually selected for plasticizers having the lowest and the highest molecular weights reported in the table. The median values are usually given for the most frequently used plasticizer (in the case of this group for di-(2-ethylhexyl) adipate).

Property	Value		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	2-ethylhexyl, butyl, butoxyethyl, heptyl, isobutyl, isodecyl, isononyl, methyl, tridecyl		
Molecular weight, daltons	174.19	510.85	342.52
NFPA health	0	1	0
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, NBR, SBR, PVAC, CAB, CP, CN, VCVAC, PS		
Main fields of application	film, cable & wire, coatings, masterbatches, nail care, belts, printer rollers, boots, gloves, aprons, tank liners, food wrap, adhesives, water pipe		
Outstanding property	low temperature resistance		
Melting point, ^{o}C	8	-70	-50
Boiling point, ^{o}C	222	509	417
Flash point, ^{o}C	145	243	192
Refractive index	1.441	1.482	1.446
Specific gravity	0.905	1.057	0.927
Vapor density	12.1	12.8	12.5
Vapor pressure at 100°C, kPa			3.9×10^{-4}
Acid dissociation constants	$pKa_1 = 4.41$, $pKa_2 = 5.28$		
Moisture content, wt%	0.02	0.1	<0.1
Solubility in water at 25°C, wt%			<0.01
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	7.31	9.64	7.61
Viscosity at 20°C, mPa s	4.8	26	13.7
Volume resistivity at 20°C, Ohm cm			2.7×10^{11}
Dielectric constant	3.55	6.15	4.13
Surface tension at 20°C, mN/m	24	33	29
Heat of vaporization at 25°C, J/g	233	294	292
Heat of combustion, kJ/kg	24,493	36,300	30,000
Cubic expansion coefficient, $10^{-4}/^{o}$C	7.6	9.3	7.8
Specific heat at 20°C, kJ/kg K	1.76	2.51	1.84
Plasticizer's loss (24 h at 87°C), wt%	2.8	27.3	8.7
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	5,000	20,500	9,110
Theoretical oxygen demand, g/g	1.75	2.85	2.63

Property	Value		
	minimum	maximum	median
Partition coefficient, log Kow			6.114
Tensile strength, 50 phr, MPa			20.1
Elongation, 50 phr,%			460
Shore A hardness, 50 phr	60	84	65
Clash-Berg temperature, 50 phr, ^{o}C			-54

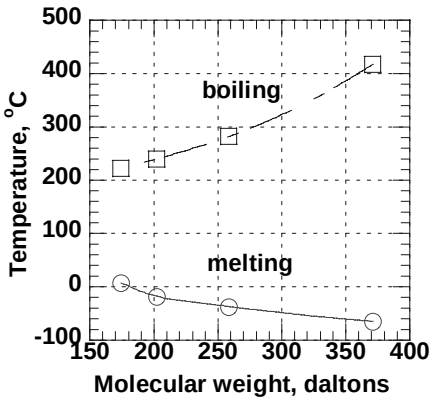


Figure 2.1. Effect of molecular weight of adipates on their boiling and melting temperatures.

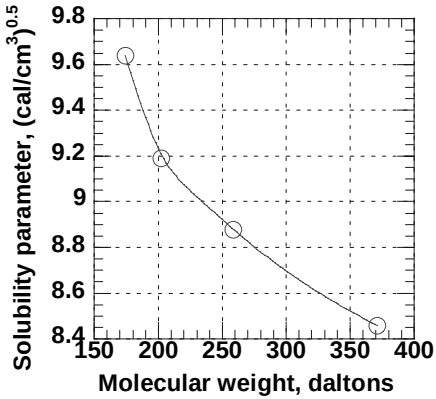


Figure 2.2. Effect of molecular weight of adipates on their Hildebrand solubility parameters.

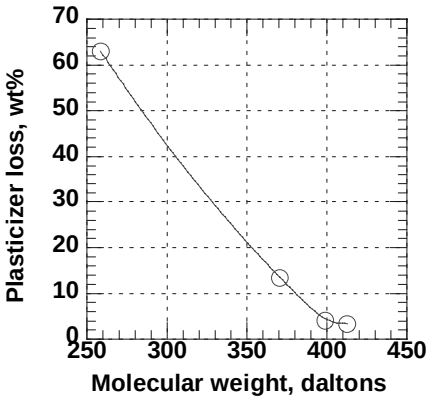


Figure 2.3 Effect of molecular weight of adipates on plasticizer loss from PVC after 24 h at 87°C. [Data from Sears J K, Darby J R, **The Technology of Plasticizers**, *John Wiley & Sons*, New York 1982.]

Esters of adipic acid constitute an important group of plasticizers. Two major applications of these plasticizers include products which perform at low temperatures and cling film.

A few comparative studies[12-14] on adipates and some other plasticizers and data available on commercial products help in generating information on the effect of chemical structure on physical properties of plasticizers. Figure 2.1 shows that melting temperature (and freezing temperature) decreases with molecular weight. Boiling point of adipates increases with increase in their molecular weight. These data show benefits of increasing molecular weight of alcohol in the plasticizer considering that

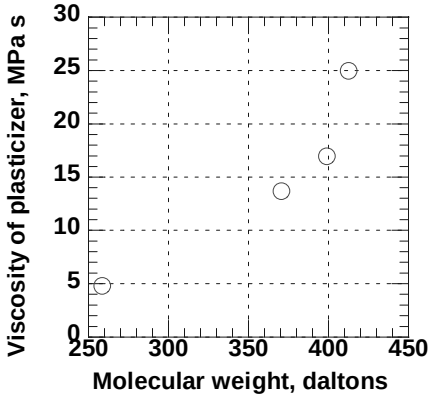


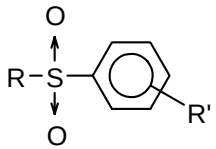
Figure 2.4. Effect of molecular weight on viscosity of adipates at 20°C.

these plasticizers are expected to be permanent additives that decrease temperature of service of plasticized articles. Figure 2.2 shows that the solubility parameter slightly decreases with an increase in molecular weight of a plasticizer. Similarly, dielectric constant of adipates decreases with their molecular weight increase. Decrease in dielectric constant parallels decrease of solvating power of a plasticizer and decrease in the solubility parameter means that difference between solubility parameter of PVC and plasticizer increases, which causes a decrease in solubility and compatibility. But, because the influence of compatibility is very small, a substantial increase in volatility sufficiently compensates the changes in compatibility and adipate plasticizers become increasingly permanent when their molecular weight increases (see Figure 2.3). The data in Figure 2.3 also explain why adipates having alcohols lower than octyl are not used in plastics. Also, it is evident that relatively high volatility of DOA can be easily decreased by the use of higher alcohols.

It should be pointed out that properties of plasticizers make their selection very easy. It was shown above that selection of plasticizers with a higher molecular weight of alcohol, improved the performance of material. Higher alcohols have little effect on the viscosity of the plasticizer (Figure 2.4). This effect is even less pronounced in PVC plastisols because adipates of higher alcohols have lower solvating strength and thus decrease the viscosity of plastisols as compared with esters with lower alcohols, which are more compatible.

2.2.3 ALKYL SULFONATES

Two plasticizers belong to this group having the following formula:



R = $C_{15}H_{31}$ and R' = H and CH_3

This traditional plasticizer has been manufactured since 1930s under the trade name of Mesamoll. Only recently Mesamoll II having lower volatility and better fogging resistance was introduced. These are improved by replacement of substituent R with paraffin of a higher molecular weight.

Property	Value
Highly recommended for these polymers	PVC, PU, NR, SBR, IIR, NBR, CR
Main fields of application	polyurethane sealants, films (automotive, tunnel linings, swimming pool covers, etc.), toys, gloves, profiles, tubing, coatings, work boots, occupational and protective clothing, waterbeds
Outstanding property	high resistance to hydrolysis; good fusion properties, good resistance to weathering
Molecular weight, daltons	~370 (Mesamoll)
Pour point, ^{o}C	-32
Flash point, ^{o}C	225
Moisture content, wt%	0.05
Viscosity at 20°C, mPa s	115-135
Dielectric constant	10.5
Plasticizer's loss (24 h at 87°C), wt%	5.3
TLV-TWA 8 h, OSHA, mg/m^3	not determined
NIOSH-IDHL, mg/m^3	not determined
Theoretical oxygen demand, g/g	2.76
Shore A hardness, 50 phr	72

2.2.4 AZELATES

Esters of azelaic acid have the following general formula:

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2(CH_2)_5CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OR$$

$$R = CH_3 \text{ to } CH_3(CH_2)_8CH_2$$

Property	Value		
	minimum	maximum	median
Main alcohols used in commercial products	methyl, ethyl, butyl, hexyl, 2-ethylhexyl, decyl, and tridecyl		
Molecular weight, daltons	216.3	468.0	412
NFPA health			1
NFPA flammability			1
NFPA reactivity			0
Highly recommended for these polymers	PVC, PS, cellulosics		
Main fields of application	food film, synthetic lubricants		

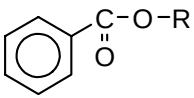
Property	Value		
	minimum	**maximum**	**median**
Outstanding property	low temperature flexibility combined with low oven loss		
Freezing point, ^oC	-18.5	-78	-78
Boiling point, ^oC	278		376
Flash point, ^oC	160	236	213
Refractive index	1.436	1.4484	1.4484
Specific gravity	1.0069	0.909	0.9167
Moisture content, wt%			0.1
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.62	8.44	8.44
Viscosity at 20^oC, mPa s			10
Dielectric constant	5.13	4.02	4.02
Plasticizer's loss (24 h at 87^oC), wt%	5.3	53.6	5.7
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg			8,720
Theoretical oxygen demand, g/g	2.07	2.74	2.72
Partition coefficient, log Kow	2.86	11.55	9.59
Shore A hardness, 50 phr	64	79	70

A wide range of azelates are available but di-(2-ethylhexyl) azelate is used in applications which require low temperature properties similar to those obtained with di-(2-ethylhexyl) adipate but with better retention of the plasticizer because of its lower volatility.

2.2.5 BENZOATES

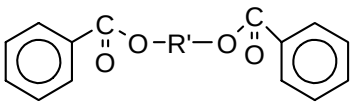
Benzoate plasticizers are either benzoates, dibenzoates, or their mixtures. Typical chemical structures are given below:

Benzoates



R = butyl, isodecyl, C_{12} - C_{15}, isodecyl, benzyl, sucrose

Dibenzoates



R' = triethylene, diethylene, and other glycols (see table below)

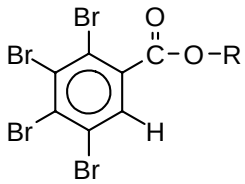
Property	Value		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	butyl, hexyl, isodecyl, alkyl C_{12}-C_{15}, benzyl, sucrose, diethylene glycol, triethylene glycol, dipropylene, glycol, 2,2,4-trimethyl,-1,3-pentandiyl glycol, 1,4-cyclohexadimethanol		
Molecular weight, daltons	178	1175	201
NFPA health	0	1	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, PVAc, PU, acrylics, SBR, PVA, EVA, alkyds, phenol-formaldehyde		
Main fields of application	wall coverings, flooring, caulks, sealants, adhesives, hot melt adhesives, powder coatings, binding agents, paints, gaskets; rolls		
Outstanding property	stain resistance, low migration		
Freezing point, ^oC	-38	90	-25
Boiling point, ^oC	249	323	321
Flash point, ^oC	148	258	174
Refractive index at 20^oC	1.49	1.569	1.49
Specific gravity at 25^oC	0.95	1.23	1.1
Vapor density	3.78	11.8	7.31
Vapor pressure at 25^oC, kPa	$2.5x10^{-8}$		$8.45x10^{-3}$
Moisture content, wt%	0.1	0.2	
Solubility in water at 25^oC, wt%	$3.04x10^{-5}$	$2.08x10^{-3}$	$6.86x10^{-4}$
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	9.61	10.06	
Viscosity at 25^oC, mPa s	15	406	80
Volume resistivity, Ohm cm			$1x10^{10}$
Dielectric constant	5.38	7.24	
Surface tension at 20^oC, mN/m			40.4
Heat of combustion, J/kg K			0.524
Cubic expansion coefficient, $10^{-4}/^oC$			6.7
Plasticizer's loss (24 h at 87^oC), wt%	1.2	11.5	8.9
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	2,661	5,313	5,000
Theoretical oxygen demand, g/g	1.96	2.42	2.2
Partition coefficient, log Kow	2.77	7.23	4.61

Property	Value		
	minimum	maximum	median
Tensile strength, 50 phr, MPa			21.5
Elongation, 50 phr,%			275
Shore A hardness, 50 phr	69	80	75

2-ethylhexyl benzoate was used as a partial replacement of DOP in plastisol formulation. It was found that benzoate plasticizer reduces viscosity of plastisol in spite of the fact that it is always considered a highly solvating plasticizer.[16,17] Use of this plasticizer also reduced gelation temperature and improved mechanical properties of vinyl sheet.

Combination of diethylene glycol dibenzoate with dipropylene dibenzoate in the nominal ratio of 50/50, results in a blend that is liquid at room temperature (diethylene glycol dibenzoate melts at about 28°C).[18,19] The same method was applied to a mixture of diethylene glycol dibenzoate and triethylene glycol dibenzoate (solidifies alone at 47°C). A mixture containing 80 wt% of diethylene glycol dibenzoate solidifies at 22°C which is below the solidification temperatures of both components.[18,19]

Brominated esters of benzoic acids were obtained, which have the following structure:

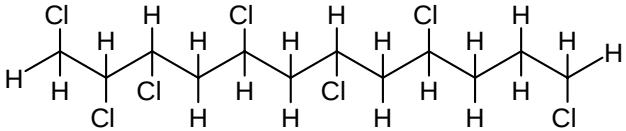


The above compound is useful as both flame retardant and plasticizer for polyesters and polyurethanes.[20]

Mono and diester of 2,2,4-trimethyl-1,3-pentanediol and benzoic acid are synthesized for applications which require excellent stain resistance.[21-23] Floor coverings and wallpaper are the major applications.

2.2.6 CHLORINATED PARAFFINS

Chemical formula below shows a structure of paraffin having 12 carbon atoms which was chlorinated to contain 60% chlorine.



Chloroparaffins are divided into 6 groups, which include:

- short chain (C_{10-13})
- intermediate chain (C_{14-17})
- long chain (C_{18-30})

Each of these groups is still divided into two classes having chlorine concentration below or above 50 wt%.[24] Each group contains a very large number of possible participating isomers which differ by the number of carbon atoms (stock dependent) and chlorine atoms (process dependent).

Property	**Value**		
	minimum	**maximum**	**median**
Molecular weight, daltons	280	1290	560
NFPA health			0
NFPA flammability			1
NFPA reactivity			0
Highly recommended for these polymers	PVC, PU, rubber, chlorinated rubber		
Main fields of application	paints, sealants, adhesives, flooring, flexible hose, cable insulation, metal-machining fluids		
Outstanding property	fire retardant action, water resistance		
Freezing point, ^{o}C	0	100	
Boiling point, ^{o}C			decomposes
Flash point, ^{o}C	210	>232	
Refractive index	1,486	1.532	1.5
Specific gravity	1.10	1.63	1.25
Vapor pressure at 20°C, kPa	$2x10^{-7}$	$3x10^{-6}$	$7x10^{-7}$
Chlorine content, wt%	40	70	50
Moisture content, wt%			<1
Solubility in water at 25°C, wt%	0.00005	0.0047	0.003
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	9.07	10.09	
Viscosity at 20°C, mPa s	70	40,000	1,000
Dielectric constant	7.82	8.59	8.09
Plasticizer's loss (24 h at 87°C), wt%	0.8	4.5	1.5
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	3,300	21,500	13,000
Theoretical oxygen demand, g/g	1.04	1.17	1.1
Partition coefficient, log Kow			6.78
Shore A hardness, 50 phr	79	100	90
Clash-Berg temperature, 50 phr, ^{o}C			-34

Figure 2.5 shows that chlorinated paraffins have a broad spectrum of molecular weights with gaussian distribution.[24] Chloroparaffins come from different manufacturers. Manufacturers use different paraffins for their production and different chlorination tech-

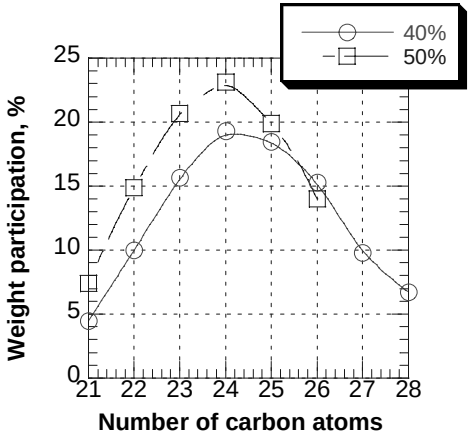


Figure 2.5. Composition of chloroparaffins (Chloroparaffin 40 and 50). [Data from Environment Health Criteria 181. Chlorinated Paraffins. United Nations Environment Programme. World Health Organization, Geneva, 1996.]

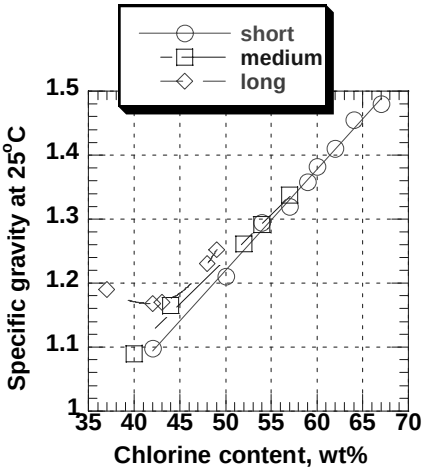


Figure 2.6. Specific gravity of short, medium, and long chain chloroparaffins containing different concentrations of chlorine. [Data from Paroil Liquid Chlorinated Paraffins, Dover Chemical Corporation.]

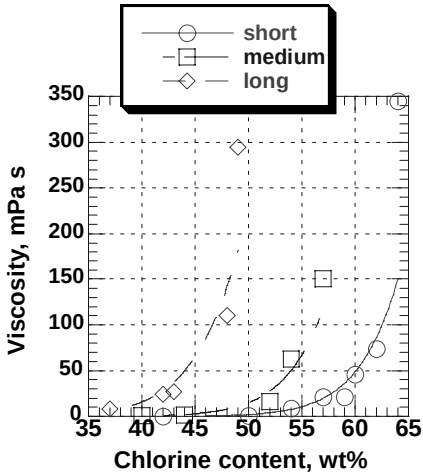


Figure 2.7. Viscosity at 25°C of short, medium, and long chain chloroparaffins containing different concentrations of chlorine. [Data from Paroil Liquid Chlorinated Paraffins, Dover Chemical Corporation.]

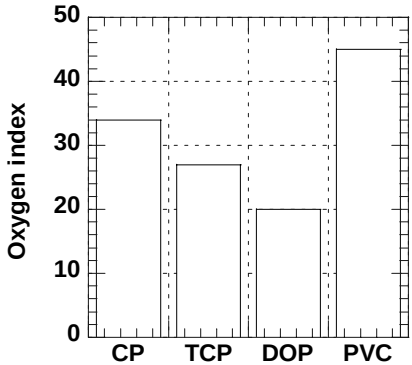


Figure 2.8. Oxygen index of PVC plastificates containing 55 phr of plasticizer. [Data from **US Patent** 4,022,812, 1977.]

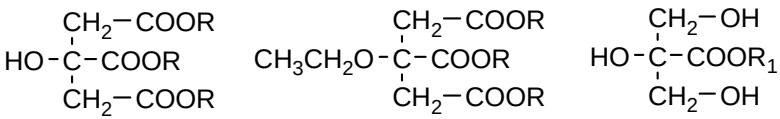
nologies. This results in formation of different products which cannot be compared based on chlorine content or general classification of chain length.

Figure 2.6 shows that specific gravity of chloroparaffin is only slightly affected by paraffin type but increases rapidly with increase in chlorine concentration.[29] This is unlike viscosity which is strongly affected by both the properties of paraffin stock and the chlori-

nation level. For chloroparaffin to be useful as a plasticizer, the substantial increase in chlorination level requires a decrease in molecular weight of paraffin, otherwise the product of chlorination becomes solid. Figure 2.8 compares the effect of chloroparaffins on fire resistance with other plasticizers. PVC without plasticizers has the best properties followed by composition containing chloroparaffin. The last one is better than tricresyl phosphate.[28]

2.2.7 CITRATES

The following chemical structures describe citrates used as commercial plasticizers:



R_1 = stearyl; R = ethyl, butyl, or hexyl

Property	Value		
	minimum	maximum	median
Main alcohols used in commercial products	ethyl, butyl, hexyl, stearyl		
Molecular weight, daltons	276	514	360.4
NFPA health			1
NFPA flammability			1
NFPA reactivity			0
Highly recommended for these polymers	PVC, cellulose, VC/VAc copolymers, CN, PVDC, PVAc, PVB, PU		
Main fields of application	cosmetics, pharmaceuticals, medical, food packaging, cigarette filters, lacquers, cling films, bottle caps, paper & aluminium foil coatings, hair sprays		
Outstanding property	considered safe in food, pharmaceutical and medical applications, some do not support fungal growth		
Freezing point, ^oC	-43	-62	-59
Boiling point, ^oC	294		
Flash point, ^oC	155	240	204
Refractive index	1.438	1.449	1.441
Specific gravity at 25^oC	1.037	1.139	1.045
Vapor pressure at 20^oC, kPa			$7.6x10^{-4}$
Moisture content, wt%	0.25	0.55	0.3
Solubility in water at 25^oC, wt%	0.1	5.5	0.65
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.60	9.04	9.02
Viscosity at 25^oC, mPa s	32	54	
Dielectric constant	4.83	7.62	6.02

Property	Value		
	minimum	maximum	median
Heat of vaporization at 25°C, J/g	221		282
Plasticizer's loss (24 h at 87°C), wt%	1.4	7	4.5
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg			32,000
Theoretical oxygen demand, g/g	1.56	2.27	1.94
Partition coefficient, log Kow	0.33	8.21	3.28
Tensile strength, 50 phr, MPa	18.9	20.5	19.7
Elongation, 50 phr,%	364	400	390
Shore A hardness, 50 phr	78	87	81

Citric acid esters are discussed in the review papers, patents, and commercial literature.[30-44] Citric acid based plasticizers are one of the major contenders to replace phthalates (especially targeted to replace DOP).[30] Some properties of materials plasticized with citrates can match those of DOP plasticized PVC but the cost of their production is substantially higher. Citrates are extracted from flexible PVC at a higher rate than DOP and trimellitates.[43] Eudragit, which is a choice polymer in pharmaceutical coatings, having controlled release or sustained release properties, performs its functions very well when plasticized with triethyl citrate.[44] The concentration of plasticizer can be used as the parameter that regulates the release rate.

2.2.8 ENERGETIC PLASTICIZERS

Energetic plasticizers are defined as the liquid materials having a positive heat of explosion. Heat of explosion is the energy released by burning the propellant or ingredient in an inert atmosphere and then cooling to ambient temperatures in a fixed volume.

Numerous plasticizers have been patented for use as energetic plasticizers in rocket propellants, pyrotechnics, explosives and munitions.[45-67]

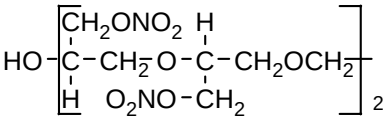
Solid propellants can be classified as being either homogeneous or composite. The former refers to the types considered true monopropellants in which each molecule contains all the necessary fuel and oxygen for combustion. The composite type propellant, in contrast, consists of a physical mixture of a fuel and an oxidizer. The homogeneous propellants are further subclassified as being either single or double base depending on whether the composition contains a single energetic combustible or contains an additional energetic combustible or a mixture of additional energetic combustibles which act as an energetic plasticizer for the first energetic combustible. Throughout this specification the first energetic combustible is referred to as the polymer, the second energetic combustible as the energetic plasticizer, and the combination of the two as the binder.[53]

The term plasticization is synonymous with gelatinization. It is used to describe the initial physico-chemical reaction of the polymer with the energetic plasticizer. By this reaction, the polymer and the energetic plasticizer form a soft colloidal dispersion. This dispersion is then made usable for propellant purposes by the application of mild heat over

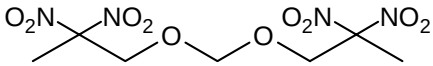
a period of time to form a tough, elastic, rubbery solid. This reaction is referred to as curing the propellant composition.[53]

If the polymer is not plasticized by energetic plasticizers, solvents must be used in the processing in order to obtain the colloidal dispersion. Solvent processes always impart a varying amount of residual volatiles in the propellant which cause the energy content to vary accordingly. Further, solvent processes require an objectionably long drying cycle and are not practical for forming most rocket propellant charges.

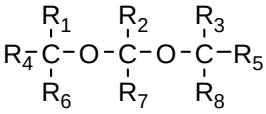
Compounds having the following formulas are used in these applications:



poly(glycidyl nitrate)

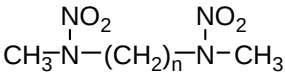


bis(2,2-dinitropropyl) formal



R_1 - R_8 = H, CH_3, or CH_3N_3

multi-azido formal



N,N'-dimethyl methylenedinitramine

It is pertinent from these structures that nitro and azide groups make plasticizers to have energetic properties. In addition to these plasticizers, also neutral plasticizers such as DOP and other plasticizers are used in these applications. The plasticizers or their combinations are selected to achieve the required effect. Inert plasticizers usually lower the energy content of polymers used in explosives (e.g., nitrocellulose).

Property	**Value**		
	minimum	**maximum**	**median**
Molecular weight, daltons	296	3,000	
Highly recommended for these polymers	hydrocarbon resins, polyesters, polyurethanes		
Main fields of application	solid propellants, pyrotechnics, explosives		
Outstanding property	low migration, low volatility, low smoke, improved storage safety, low temperature properties, electrostatic insensitivity, low toxicity		
Freezing point, ^{o}C	-60	75	
Specific gravity	1.29	1.47	
Heat of combustion, kJ/kg	-18.45	-6970	
Tensile strength, 5 phr, MPa	0.75	0.92	
Elongation, 5 phr,%	31	49	

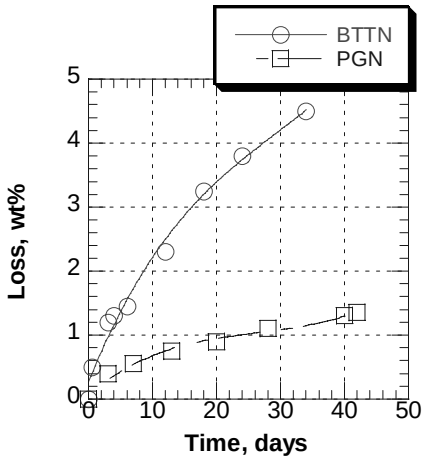


Figure 2.9. Loss of plasticizer under vacuum of 0.2 mm Hg. PGN - poly(glycidyl nitrate), BTTN - 1,2,4-butane triol trinitrate. [Data from Willer R, Stern A G, Day R S, **US Patent** 5,380,777, 1995.]

Plasticizers are usually incorporated into energetic compositions as processing aids to improve the workability, flexibility, and/or distensibility of the binder of the composition. These improvements are accomplished by, for example, altering mechanical properties such as glass transition temperature or formulation viscosity.[47]

One of the best known energetic plasticizers is nitroglycerine. It is well known for its use with nitrocellulose in double-base and triple-base propellants and explosive powders. A significant drawback shared by nitroglycerine and other nitrate ester-containing molecules, and polyolpolynitrates, such as diethyleneglycol-dinitrate and triethyleneglycol-dinitrate, is their poor thermal stability and high shock sensitivity, which make compositions containing such plasticizers dangerous to handle and extremely prone to accidental detonation.[47]

Energetic plasticizers tend to be somewhat viscous in nature, and this limits the amount of solids that can be included in propellant formulations while maintaining good propellant processability. Reducing the solids loading of a propellant generally results in a lowered propellant impulse.[49]

It is also known that some plasticizers (e.g., ferrocene and the ferrocene derivatives) have a tendency to oxidize and to migrate over time towards the surface of the propellant, and sometimes even to sublimate. The plasticizer migration causes irregularities in combustion.[50] Because of the tendency of plasticizer molecules to migrate or evaporate out of the propellant composition during storage the chemical changes in the composition occur which are harmful to the propellant and to other inert parts of the rocket motor.[57]

Figure 2.9 shows a plot of the percent weight loss of a poly(glycidyl nitrate) plasticizer, PGN, and of 1,2,4-butane triol trinitrate, BTTN, versus time at an average vacuum of 0.2 mm Hg. This vacuum is equivalent to an altitude greater than 61,500 m. The PGN nitrate loses very little weight (>2%) in 43 days while the BTTN has suffered a substantial weight loss in the same time period.[45]

Compounds such as adiponitrile, triacetin, dibutyl phthalate are very good plasticizers but are inert and actually lower the energy content of the nitropolymer. On the other hand, compounds such as diethyleneglycoldinitrate, 1,1,1-trimethylolethanetrinitrate, nitroisobutyltrinitrate, and nitroglycerin contribute energy but they have the undesirable characteristics associated with nitrate esters; toxicity (headache potential), volatility, low thermal stability and high shock sensitivity. Nitroglycerin shows these undesirable properties to the greatest extent.[63] Electrostatic sensitivity is also one of the major concerns.[63]

In using solid propellants, a problem exists in that an undesirable amount of smoke is often produced in the exhaust gases emanating from the solid rocket motor during propul-

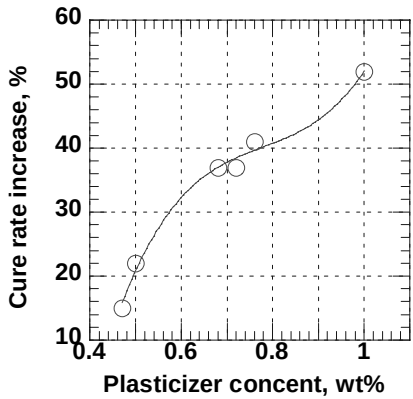


Figure 2.10. Effect of ferrocene plasticizer on cure rate increase of epoxide-cured polybutadiene acrylic acid copolymer. [Data from Arendale W F, **US Patent** 4,023,994, 1977.]

sion. Excessive amounts of smoke are extremely undesirable in the exhaust gases since this provides data which help to locate the sites from which the missiles or rockets are being fired.[65]

Plasticizers require excellent physical compatibility and greater safety at elevated temperatures during production, handling and use.[50] Low temperatures also have an effect on these materials. If a plasticizer crystallizes solid propellant becomes brittle and has a tendency to crack, which causes irregular burning properties.[51] Plasticizers often affect curing rate of binder as seen in Figure 2.10.[66]

Many previous and current studies aim at elimination of various disadvantages of plasticizers but so far energetic plasticizers are under continuous development.

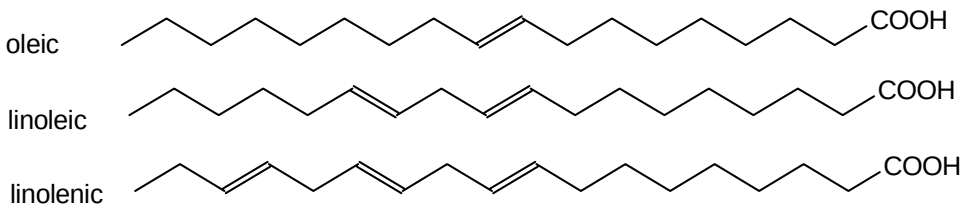
2.2.9 EPOXIDES

Three oils are frequently used as raw materials for manufacture of epoxy plasticizers. Composition of fatty acids of these oils is given in Table 2.3.

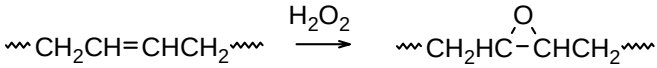
Table 2.3. The average composition of major fatty acid components in oils frequently used in epoxy plasticizers

	Soybean oil	Linseed oil	Tall oil
	Average composition, wt%		
Palmitic	12	5.3	1.6
Stearic	5	3.5	2.2
Oleic	26	19.5	42.3
Linoleic	52	14.6	34.8
Linolenic	6	56.2	

Three acids in Table 2.3 are unsaturated:



These unsaturated acids can be epoxidized with the use of hydrogen peroxide or peracetic acid, according to the following reaction scheme:



Typical concentrations of oxirane oxygen are as follows:

epoxidized soybean oil	5.5-7%
epoxidized linseed oil	9%
epoxidized tall oil	4.7%
octyl epoxy stearate	3.5%

Property	**Value**		
	minimum	**maximum**	**median**
Main acids used in commercial products	oleic, linoleic, linolenic		
Molecular weight, daltons	420	1,000	1,000
NFPA health	0	1	0
NFPA flammability	0	1	0
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, PVB, PVA emulsion, chlorinated rubber, NC, EC		
Main fields of application	cables, foils, films, sheets, coated fabrics, upholstery, wallcoverings, flooring, tubes, pipes, blood bags, bottles, food wrap, medical, food		
Outstanding property	improves resistance to heat and UV, low migration, low toxicity		
Freezing point, ^{o}C	-22	0	-22
Boiling point, ^{o}C	260	decomposes	decomposes
Flash point, ^{o}C	215	343	260
Refractive index at 25°C	1.457	1.472	1.465
Specific gravity at 20°C	0.927	1.04	0.96
Vapor density			25
Vapor pressure at 20°C, kPa	0.00133	0.0133	
Oxirane oxygen content, wt%	3.5	9	7
Moisture content, wt%			0.03
Solubility in water at 25°C, wt%			0.01
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.8	8.91	8.9
Viscosity at 20°C, mPa s	20	880	580
Volume resistivity, Ohm cm			$8x10^{13}$
Dielectric constant	4.17	6.57	5.49
Plasticizer's loss (24 h at 87°C), wt%	0.3	0.9	0.6

Property	Value		
	minimum	maximum	median
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	2,000	22,500	5,000
Theoretical oxygen demand, g/g	2.41	2.88	2.55
Tensile strength, 50 phr, MPa	17.3	19.08	18.1
Elongation, 50 phr,%	377	405	390
Shore A hardness, 50 phr	63	78	75
Clash-Berg temperature, 50 phr, ^oC			-11

A continuous search for plasticizers which may replace phthalates has created renewed interest in epoxy plasticizers because they are considered non-toxic alternatives.[68-71] In the production of toys, epoxidized soybean oil alone and in combination with citrates is considered as a suitable replacement for phthalates.[68]

Other sources of oils which may be epoxidized are also studied, especially palm oil which is readily available in Asia and Africa.[69] Modification of epoxidized soybean oil is also studied to develop grades which lower concentration of this plasticizer and have retention of mechanical properties obtainable with DOP.[70]

2.2.10 GLYCOL ETHERS AND THEIR ESTERS

This is a very broad group containing monomeric and polymeric compounds which may be classified as plasticizers or, in some cases, as slow evaporating solvents. The following chemical formulas describe structures of these materials:

$H(OCH_2CH_2)_nOH$

polyethylene glycols

$H(OCH_2CH_2CH_2)_nOH$

polypropylene glycols

$RC(=O)(OCH_2CH_2)_nOC(=O)R$

n = 3, R = acetate, caprylate, caproate, 2-ethylhexylate

Polyethylene and polypropylene glycols are used as monomers (n=1), oligomers (diethylene, dipropylene, n=2; triethylene, tripropylene, n=3; and tetraethylene, tetrapropylene, n=4) and higher molecular weight glycols. Increased number of monomeric units increases almost linearly boiling point (see Figure 2.11) and the solvent becomes a plasticizer when n becomes larger than three (boiling point increases above 250°C).

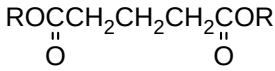
Property	Value		
	minimum	maximum	median
Main acids used in commercial products	acetic, mixed (average C_9), caprylic (octanoic), 2-ethylhexyl, capric (decanoic)		
Molecular weight, daltons	150	1,000	286

Property	Value		
	minimum	**maximum**	**median**
NFPA health	0	1	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, PVAc, PVB, PU, NBR, SBR, CR, CTA, EPDM, EVA, acrylics, cellulose derivatives, polyesters		
Main fields of application	electronic applications, cable coatings, printing inks, pharmaceuticals, cosmetics, floor tiles, paints, coatings, automotive, glues		
Outstanding property	low viscosity, low temperature flexibility		
Freezing point, ^{o}C	-6	-70	-40
Boiling point, ^{o}C	245	344	280
Flash point, ^{o}C	145	204	160
Refractive index	1.432	1.460	1.45
Specific gravity	0.941	1.129	1.11
Vapor density	2.6	5.1	3.3
Vapor pressure at 100°C, kPa	1.72×10^{-7}	0.017	0.01
Moisture content, wt%	0.05	0.5	0.2
Solubility in water at 25°C, wt%	0.01	complete	
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.51	9.48	8.9
Viscosity at 20°C, mPa s	12	140	35
Volume resistivity, Ohm cm			3×10^{6}
Dielectric constant	6.59	37.7	
Surface tension at 20°C, mN/m	33	45	35
Heat of combustion, kJ/kg	19,180	24,000	
Cubic expansion coefficient, $10^{-4}/^{o}$C	8.1×10^{-4}	8.5×10^{-4}	
Specific heat at 20°C, kJ/kg K	1.2087	2.8	
Thermal conductivity at 25°C, W/m K			0.2092
Plasticizer's loss (24 h at 87°C), wt%	7.0	36.9	11.5
TLV-TWA 8 h, OSHA, mg/m^{3}	not determined		
NIOSH-IDHL, mg/m^{3}	not determined		
LD50, acute - rat oral, mg/kg	3,200	20,400	12,565
Theoretical oxygen demand, g/g	1.6	2.4	2.0
Partition coefficient, log Kow	-2.02	6.73	
Shore A hardness, 50 phr	60	74	67
Clash-Berg temperature, 50 phr, ^{o}C	-57	-65	-62

Figure 2.12 shows that polypropylene glycol performs in a typical way by reducing tensile strength of material. Elongation increases when amount of plasticizer increases.[72]

2.2.11 GLUTARATES

Diesters of glutaric acid have the following formula:



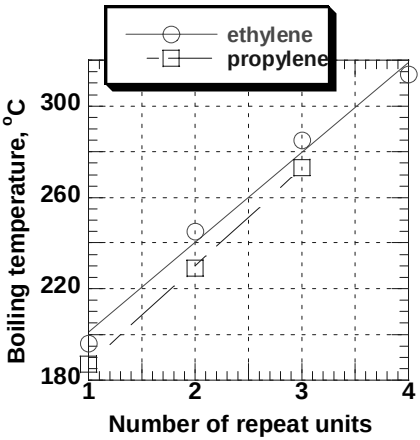


Figure 2.11. Boiling temperatures of polyethylene and polypropylene glycols having different number of monomeric units.

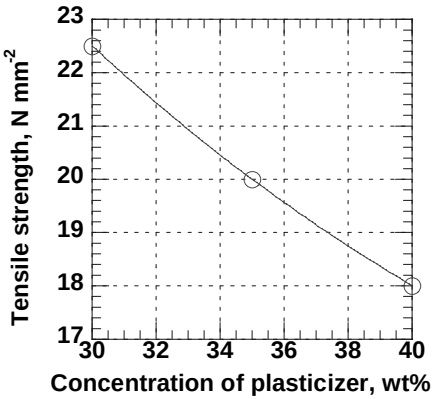


Figure 2.12. Tensile strength of zein films plasticized with different concentrations of polypropylene glycol. [Data from Tillekeratne M; Easteal A J, *Polym. Intl.*, **49**, No.1, Jan.2000, p.127-34.]

Structure and properties of these plasticizers are similar to two groups of plasticizers: adipates and sebacates. The main advantages of these plasticizers are their low temperature properties. There are two reasons for lower interest in glutarates. Low molecular weight, compared with adipates makes their volatilization and migration even more likely. Synthesis of adipic acid is part of polyamide production. Adipic acid of high purity can be obtained as a product of cyclohexane oxidation. Depending on the rate of oxidation, mixtures of acids, such as adipic, glutaric and succinic can be obtained which are then used as a feedstock for synthesis of monomeric or polymeric plasticizers. Glutaric acid is more frequently used in the synthesis of polymeric (see Section 2.18) than monomeric plasticizers. Lower esters (methyl, ethyl) have boiling temperatures below 250°C (limit for plasticizers).

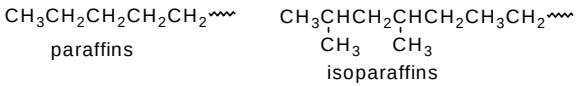
Property	**Value**		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	isodecyl, 2-ethylhexyl		
Molecular weight, daltons	384.6	412.6	
NFPA health			1

Property	Value		
	minimum	**maximum**	**median**
NFPA flammability			1
NFPA reactivity			0
Highly recommended for these polymers	PVC, NBR, SBR, PVAc, CAB, CP, CN, VC/VAc, PS, acrylics		
Main fields of application	adhesives, sealants, coatings, cosmetics		
Outstanding property	low temperature flexibility		
Boiling point, ^oC	260	280	
Flash point, ^oC	110	193	
Refractive index	1.447	1.449	
Specific gravity at 25^oC	0.92	1.06	
Moisture content, wt%			0.2
Dielectric constant	2.43	4.00	
Plasticizer's loss (24 h at 87^oC), wt%			28.7
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
Shore A hardness, 50 phr			62
Clash-Berg temperature, 50 phr, ^oC			-67

2.2.12 HYDROCARBON OILS

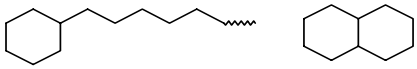
The following chemical formulas characterize the components of various types of oils:

Paraffinic oils



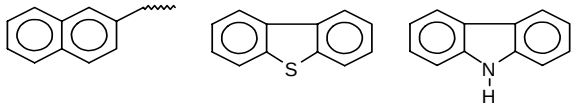
paraffins isoparaffins

Naphthenic oils



derivatives of cyclohexane or decalin

Aromatic oils



derivatives naphthalene, dibenzothiophene, carbazole, etc.

These three groups of oils have unique properties which depend on a source of crude and processing method. Table 2.4 shows general composition of some crude oils.

Table 2.4. Typical characteristics of some crudes.

Source	Paraffins, vol%	Aromatics, vol%	Naphthenes, vol%	Sulfur, wt%
Nigeria, light	37	9	54	0.2
Saudi, light	63	19	18	2
Saudi, heavy	60	15	25	2.1
Venezuela, light	52	14	34	1.5
Venezuela, heavy	35	12	53	2.3
North Sea	50	16	34	0.4

In addition to these characteristics, the molecular weight of components of different fractions vary, which affects compositions of heavier fractions such as oils. ASTM D2226 gives the following classification oils (Table 2.5).

Table 2.5. Oil classification according to ASTM D2226

Oil type	Asphaltenes, % max	Polar compounds, % max	Saturates, %
Aromatic 101	0.75	25	20 (max)
102	0.5	12	20.1-35.1
Naphthenic 103	0.3	6	35.1-65
Paraffinic 104	0.1	1	65 (min)

The amount of asphaltenes determines toxicity (aromatic oils are substantially more toxic than naphthenic and paraffinic). Presence of asphaltenes determines potential use in different polymeric materials. In addition to these characteristics, concentration of impurities such as sulfur and nitrogen are important because they affect oxidation and UV degradation. Very pure paraffinic oils are the most stable compounds.

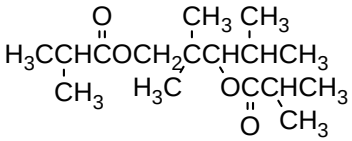
Mineral oils are always mixtures of components but their name indicates which fractions are prevalent.

Property	Value		
	paraffinic	naphthenic	aromatic
Molecular weight, daltons	254-890	290-490	
NFPA health	0	0	
NFPA flammability	1	1	
NFPA reactivity	0	0	
Highly recommended for these polymers	natural rubber, EPDM; EP, SBR, PVC		
Main fields of application	sealants, coatings, degreasers, road marking paints, medical		

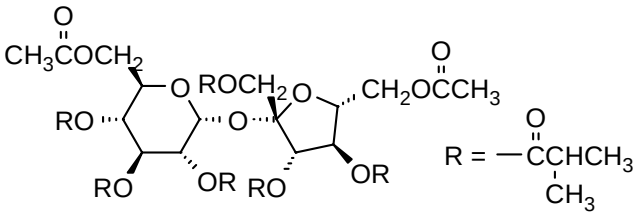
Property	Value		
	paraffinic	**naphthenic**	**aromatic**
Outstanding property	UV and color stability (paraffinic & naphthenic), low volatility, low cost		
Freezing point, ^{o}C	-7 to -21	-6 to -45	10 to -38
Boiling point, ^{o}C	above 250, dec	above 250, dec	above 250
Flash point, ^{o}C	204-310	164-248	210-245
Refractive index	1.433-1.4916	1.480-1.508	1.522-1.598
Specific gravity	0.797-0.9	0.880-0.924	1.035-1.13
Vapor density	>1	>1	
Vapor pressure at 100°C, kPa		0.16	
Sulfur content, wt%		0.01-1	
Aromatic content, wt%	<1	1-13	41
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	6.9-8.0		8.6-9.8
Aniline point, ^{o}C	90-120	55-110	22-55
Dielectric constant	2.1-4.5		
Surface tension at 20°C, mN/m	25-37		
Heat of combustion, kJ/kg	79,000-80,000	78,000-79,000	70,000-76,000
Plasticizer's loss (22 h at 107°C), wt%	0.01-0.8	0.1-18	
TLV-TWA 8 h, OSHA, mg/m^3	5	5	5
NIOSH-IDHL, mg/m^3	2,500	2,500	2,500
LD50, acute - rat oral, mg/kg	>5000	>5000	
Theoretical oxygen demand, g/g	3.4	3.4	
Partition coefficient, log Kow		>6	
Shore A hardness, 50 phr	76		78

2.2.13 ISOBUTYRATES

The following formulas give examples of isobutyrate plasticizers:



2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB)



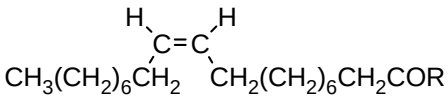
sucrose diacetate hexaisobutyrate

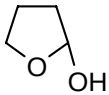
Property	Value		
	TXIB	**sucrose**	**sucrose + solvent**
Main alcohols used in commercial products	propane diol, sucrose		
Molecular weight, daltons	286.4	847	847
NFPA health	0	0	1-2
NFPA flammability	1	1	3
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVAc, acrylic, CA, CN, CAB, CTA		
Main fields of application	cosmetics, hair care products, nail care products, beverage emulsions, lacquers, printing inks, textiles, vinyl flooring, toys		
Outstanding property	low toxicity and low volatility (sucrose ester)		
Freezing point, ^{o}C	-70	-7	-83
Boiling point, ^{o}C	281.5	288 (decomp)	78-105
Flash point, ^{o}C	128	260	15.9-21.5
Refractive index at 20°C	1.434	1.454	
Specific gravity at 25°C	0.942-0.948	1.146	1.09-1.11
Vapor density			1.5
Vapor pressure at 20°C, kPa			5.32
Solubility in water at 25°C, wt%	0.42		
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.20		

Property	Value		
	TXIB	**sucrose**	**sucrose + solvent**
Viscosity at 25°C, mPa s	9		750-1000
Volume resistivity, Ohm cm		$1x10^{15}$	
Dielectric constant	4.78		
Surface tension at 20°C, mN/m	$2.756x10^{-3}$		
Plasticizer's loss (24 h at 87°C), wt%	27.3	0.5	
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg		22,600	
Theoretical oxygen demand, g/g	2.40	1.83	
Partition coefficient, log Kow	4.91	5.03	
Shore A hardness, 50 phr	76		
Clash-Berg temperature, 50 phr, °C	-33		

2.2.14 OLEATES

The following formula characterizes structure of oleate plasticizers:



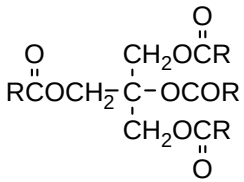
R = $CH_3(CH_2)_3$, $CH_3(CH_2)_3OCH_2CH_2$, 

Property	Value		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	butyl, butoxyethyl, furfuryl		
Molecular weight, daltons	338.6	382.6	366.6
NFPA health			1
NFPA flammability			1
NFPA reactivity			0
Highly recommended for these polymers	PVC, natural & synthetic rubber		
Main fields of application	coatings, films, inks, film, sheet, leather, hose, flooring		
Outstanding property	low temperature flexibility, stable viscosity		
Freezing point, °C	-27	-35	-28

Property	Value		
	minimum	maximum	median
Boiling point, ^{o}C			395
Flash point, ^{o}C	185		198
Refractive index	1.455	1.462	
Specific gravity	0.862	0.928	0.88
Vapor pressure at 200°C, kPa	0.13	0.5	0.3
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.15	8.39	
Viscosity at 20°C, mPa s	8.2	9.4	
Dielectric constant	3.21	4.47	3.68
Surface tension at 20°C, mN/m	30	34	33
Heat of combustion, kJ/kg			40,146
Specific heat at 20°C, kJ/kg K			2.55
Plasticizer's loss (24 h at 87°C), wt%			11.0
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
Theoretical oxygen demand, g/g	2.79	2.97	2.84
Partition coefficient, log Kow	9.21	9.49	
Shore A hardness, 50 phr			72
Clash-Berg temperature, 50 phr, ^{o}C	-51	-67	

2.2.15 PENTAERYTHRITOL DERIVATIVES

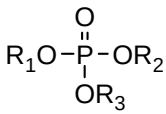
The following formula characterizes structure of pentaerythritol plasticizers:



Property	Value		
	minimum	maximum	median
Main acids used in commercial products	benzoic,[74,76] butyric, mixture of C_5, C_7, C_9 alkanoic acids,[75,77,78] fatty acids		
Molecular weight, daltons	538.3	818.3	552.55
NFPA health			1
NFPA flammability			1

Property	Value		
	minimum	**maximum**	**median**
NFPA reactivity			0
Highly recommended for these polymers	PVC, PEI, rubber		
Main fields of application	cable & wire, thin-wall articles, plastisols		
Outstanding property	low temperature flexibility, oxidative stability, reduced smoke density		
Freezing point, ^{o}C	-60	102	
Flash point, ^{o}C	268	300	
Refractive index	1.455	1.543	1.455
Specific gravity	0.97	1.02	
Viscosity at $20^{o}C$, mPa s	50	110	85
Volume resistivity, Ohm cm	$1.0x10^{12}$	$9.0x10^{13}$	
Dielectric constant			5.29
Plasticizer's loss (24 h at $87^{o}C$), wt%	1.1	2.1	
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
Tensile strength, 50 phr, MPa			19.3
Elongation, 50 phr,%			310
Shore A hardness, 50 phr	72	90	74
Clash-Berg temperature, 50 phr, ^{o}C	-10	-34	-28

2.2.16 PHOSPHATES



R_1, R_2, R_3 - the same or mixed

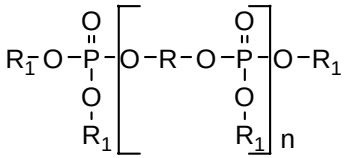
Property	Value		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	isopropanol, butanol, butoxyethanol, 2-ethylhexyl, isodecyl, phenol, cresol, xylenol, 2-chloroethanol		
Molecular weight, daltons	266	434	320
NFPA health	0	2	1
NFPA flammability	1	1	1
NFPA reactivity	0	1	0

Property	Value		
	minimum	**maximum**	**median**
Highly recommended for these polymers	PVC, PVAc, PS, PMMA, PP, PF, PA, PE, acrylics, nitrocellulose, cellulosic resins, EP, EC, NBR, SBR, natural rubber, PU, phenolic resins, CA, NC, ABS/PC, PPO blends (with HIPS and other polymers),		
Main fields of application	film, foams, paper coatings, textile coatings, latex paints, lacquers, sheet goods, wire, cable, tubing, sealants, printed circuit boards, photographic base film, synthetic leather, wall coverings, flooring, tarpaulins		
Outstanding property	flame retardant, low smoke		
Freezing point, ^{o}C	8	-90	
Boiling point, ^{o}C	289 decomp	420	
Flash point, ^{o}C	93.5	263	220
Refractive index	1.441	1.564	
Specific gravity at 20°C	0.98	1.30	1.16
Vapor density	12.7	14.95	
Vapor pressure at 100°C, kPa	0.0001	0.03066	
Phosphorus content, wt%	5.3	11.7	8.6
Moisture content, wt%	0.1	0.2	
Solubility in water at 25°C, wt%	<0.0008	<0.001	
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.25	10.36	9.3
Viscosity at 20°C, mPa s	15	100	
Dielectric constant	4.35	7.84	6.97
Surface tension at 20°C, mN/m	25	44	38
Heat of vaporization at 25°C, J/g	191	430	245
Heat of combustion, kJ/kg	22,585	32,494	30,500
Cubic expansion coefficient, $10^{-4}/^{o}$C	0.0005	0.00086	0.00067
Specific heat at 20°C, kJ/kg K	1.39	2.42	1.72
Thermal conductivity at 25°C, W/m K	0.122	0.130	
Plasticizer's loss (24 h at 87°C), wt%	1.6	11.0	3.6
TLV-TWA 8 h, OSHA, mg/m^3	0.1	5	
NIOSH-IDHL, mg/m^3	40	1,000	
LD50, acute - rat oral, mg/kg	3,000	14.750	
Theoretical oxygen demand, g/g	1.21	2.65	2.16
Partition coefficient, log Kow	1.63	9.07	4.7
Tensile strength, 50 phr, MPa	13.0	17.7	
Elongation, 50 phr, %	301	437	
Shore A hardness, 50 phr	65	84	70

Property	Value		
	minimum	maximum	median
Clash-Berg temperature, 50 phr, ^{o}C	-9	-56	-32

Aryl, alkyl, and mixed esters of phosphoric acid are used as plasticizers. Aryl esters are preferred as flame retarding components of formulation. Aryl plasticizers have low volatility and good extraction resistance but they decrease low temperature flexibility. Alkyl phosphates are good low temperature plasticizers but less effective as flame retarding additives. Each product manufactured requires plasticizers having a certain combination of properties and this is one of the reasons why so many plasticizers are produced.

Volatility and non-fogging are other properties that have to be developed by a proper method of production or composition. A plasticizer having a low volatility is obtained by passing a mixture of reacted products through a thin film evaporator at temperature in the range of 200-250 under pressure lower than 5 kPa and evaporation of 5 to 30% of the composition.[80] In automotive applications, where fogging is the major concern, plasticizers based on organic diphosphates are used (n=1):



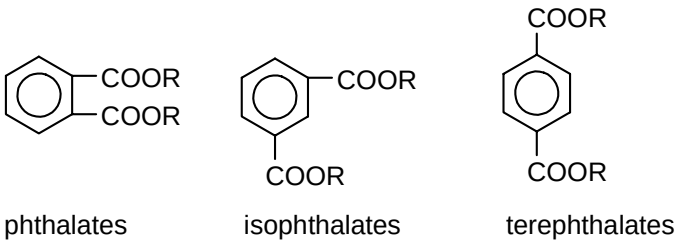
Use of this plasticizer, which is commercially available (Fyrolflex RDP) permits to obtain, non-fogging, flame retarded polyurethane foam.[79] Incorporation of halide (preferably chlorine) in trialkyl plasticizer results in an ignition resistant, UV stable plasticizer.[81]

Effect of a plasticizer on heat stability of PVC, flexibility of plasticized material at room and low temperatures is usually balanced by the selection of a required proportion between aryl and alkyl components.[85] Low temperature properties can be improved by alkylphenylation with special attention to isopropyl substituents.[86] Also haze can be eliminated in PVC composition by use of alkylated derivatives (e.g., methylphosphonate).[87]

Many efforts were made by international groups of specialists to analyze reasons for increased toxicity of some phosphates such as tricresyl and triphenyl phosphates. Their extensive findings are reported elsewhere.[91,92]

2.2.17 PHTHALATES

There are three isomeric forms of phthalic acids and as many phthalates as shown below:



Out of these three groups, phthalates, which are esters of ortho-phthalic acid, are popular (in fact, they constitute about 80% of all plasticizers used). Esters of two other acids are seldom used because of the higher prices of these acids.

Property	**Value**		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	methyl, ethyl, butyl, isobutyl, hexyl, cyclohexyl, heptyl, octyl, 2-ethylhexyl, 1-methylheptyl, butoxycarbonylmethyl, nonyl, isononyl, decyl, isodecyl, undecyl, tridecyl, benzyl, mixtures of alcohols (e.g., C_7 to C_9 or C_9 to C_{11}, etc.), 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate		
Molecular weight, daltons	194.2	530	390.6
NFPA health	0	2	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, CA, CN, PVAc, PU, EC, EPDM, PMMA, PS, acrylics, cellophane, nitrocellulose, natural & synthetic rubber, chlorinated rubber, polysulfide		
Main fields of application	automotive, cable & wire, coatings, flooring, sheeting, film, tubing, extruded profiles, sealants, adhesives, bottle caps, gloves, upholstery, nail care, sporting goods, medical, food wrappers, electronics, toys, inks, coated fabrics, carpet backing, shoes, gaskets, foam		
Outstanding property	compatibility, cost effectiveness, good dielectric properties, UV & thermal stability, a broad range of properties, good balance of properties		
Freezing point, ^oC	0	-58	-50
Boiling point, ^oC	283	523	384
Flash point, ^oC	146	254	216
Refractive index	1.481	1.515	1.486
Specific gravity at 20^oC	0.948	1.191	0.977
Vapor density	6.69		13.5
Vapor pressure at 100^oC, kPa	$3.0x10^{-8}$	0.12	$1.8x10^{-4}$
Moisture content, wt%	0.02	0.2	0.1
Solubility in water at 25^oC, wt%	$3.0x10^{-7}$	$1.2x10^{-3}$	$<1.0x10^{-3}$
Hildebrand solubility parameter, $(MPa)^{0.5}$		22.1	16.83
Viscosity at 20^oC, mPa s	11	320	78
Volume resistivity, Ohm cm	$1.0x10^9$	$1.0x10^{12}$	$2.0x10^{10}$
Dielectric constant	4.06	8.49	4.9
Surface tension at 20^oC, mN/m	32.1	43.2	33

Property	Value		
	minimum	maximum	median
Heat of vaporization at boiling point, J/g	207	283	235
Heat of combustion, kJ/kg	24,371	37,425	35,471
Cubic expansion coefficient, 10^{-4}/°C	7.5×10^{-4}	8.010^{-4}	7.8×10^{-4}
Specific heat at 20°C, kJ/kg K	1.57	1.803	1.75
Thermal conductivity at 25°C, W/m K	0.127	0.144	0.135
Plasticizer's loss (24 h at 87°C), wt%	0.8	31	3.6
TLV-TWA 8 h, OSHA, mg/m^3	5	5	5
NIOSH-IDHL, mg/m^3	2,000	5,000	
LD50, acute - rat oral, mg/kg	6,890	30,600	
Theoretical oxygen demand, g/g	1.73	2.81	2.58
Partition coefficient, log Kow	1.66	12.25	8.39
Tensile strength, 50 phr, MPa	18.0	24.1	24.1
Elongation, 50 phr, %	320	350	341
Shore A hardness, 50 phr	73	90	78
Brittle temperature, 50 phr, °C	-38	-43	-39

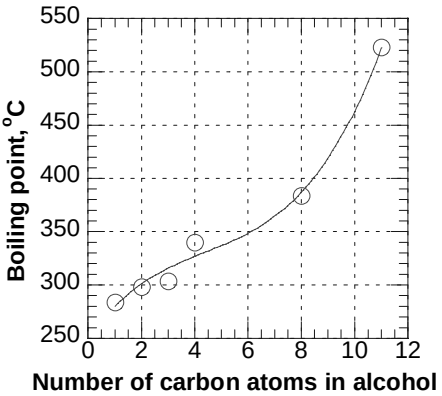


Figure 2.13. Boiling temperatures of esters of phthalic acid and alcohols having different number of carbon atoms.

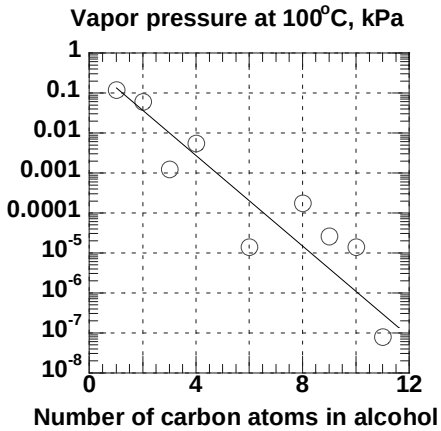


Figure 2.14. Vapor pressures at 100°C of esters of phthalic acid and alcohols having different number of carbon atoms.

Long experience with phthalates and a large number of plasticizers having different molecular weight of their alcohol parts allowed for generation of comprehensive information which may be discussed to characterize effect of alcohol in plasticizer on its physical, chemical, and mechanical properties. Figure 2.13 shows that boiling temperature increases when number of carbon atoms in alcohol (or molecular weight) increases. The increase in

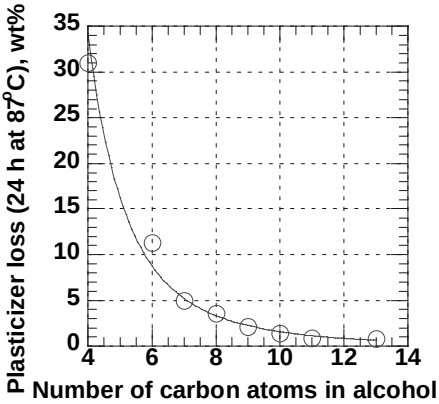


Figure 2.15. Loss of esters of phthalic acid and alcohols having different number of carbon atoms during 24 h at 87°C from plasticized PVC containing 50 phr plasticizer.

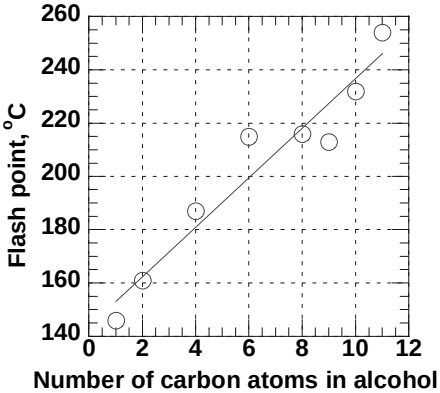


Figure 2.16. Flash points of esters of phthalic acid and alcohols having different number of carbon atoms.

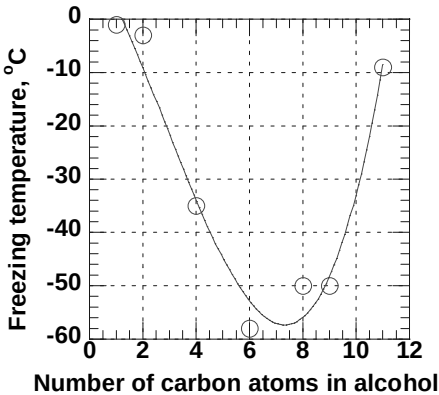


Figure 2.17. Freezing temperatures of esters of phthalic acid and alcohols having different number of carbon atoms.

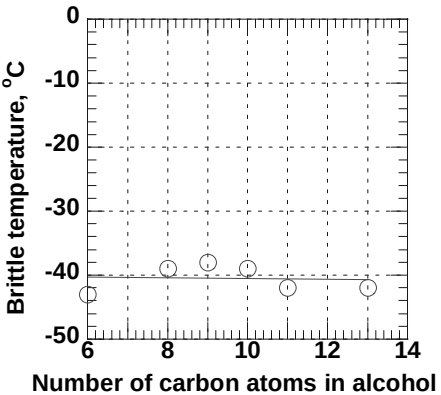


Figure 2.18. Brittle temperatures of PVC plasticized with 50 phr of esters of phthalic acid and alcohols having different number of carbon atoms.

boiling temperature causes decrease in vapor pressure of plasticizer (Figure 2.14) and this is the most important influence on plasticizer retention which increases with increase in molecular weight of plasticizer (Figure 2.15). It should be underlined that the results presented here are for the same chemical structure of plasticizers which, thus, have a similar interaction with the polymer, therefore these plasticizers are mostly influenced by their molecular weights. With different acids, compatibility and potential interactions change

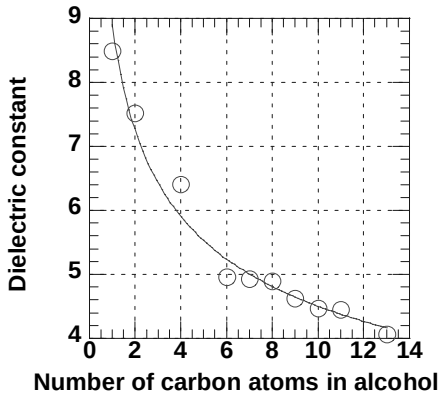


Figure 2.19. Dielectric constants of esters of phthalic acid and alcohols having different number of carbon atoms.

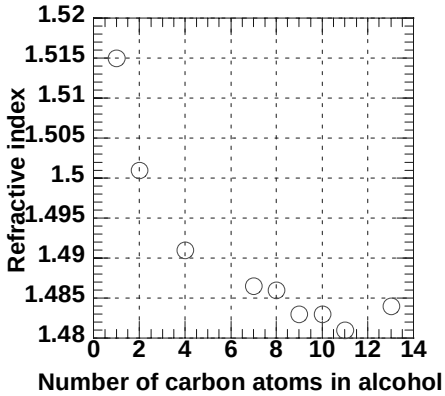


Figure 2.20. Refractive indices of esters of phthalic acid and alcohols having different number of carbon atoms.

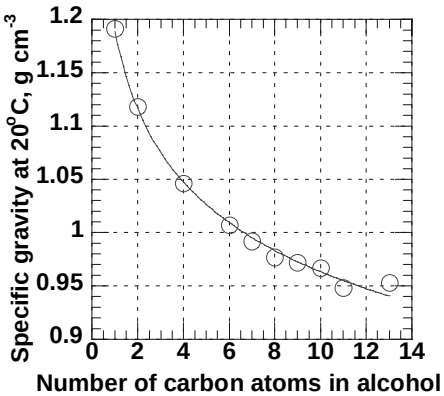


Figure 2.21. Specific gravities of esters of phthalic acid and alcohols having different number of carbon atoms.

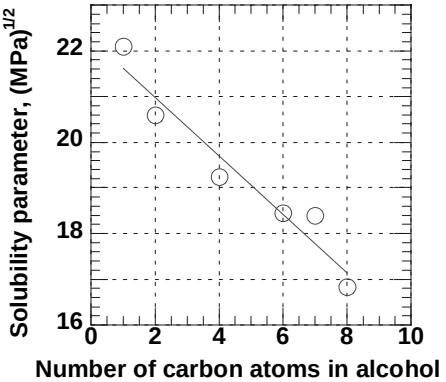


Figure 2.22. Hildebrand solubility parameters of esters of phthalic acid and alcohols having different number of carbon atoms.

but general influence of molecular weight also remains valid. Flash point of plasticizers follows a similar relationship (Figure 2.16).

Figure 2.17 shows influence of number of carbon atoms in alcohol on freezing temperature of plasticizer. The relationship is non-linear and plasticizers having six to nine carbon atoms have the lowest freezing points. It is interesting to note that low temperature properties of plasticized PVC depend on the type of acid used for plasticizer production rather than the molecular weight of alcohol. Molecular weight of alcohol does not seem to influence brittle temperature of plasticized PVC (Figure 2.18).

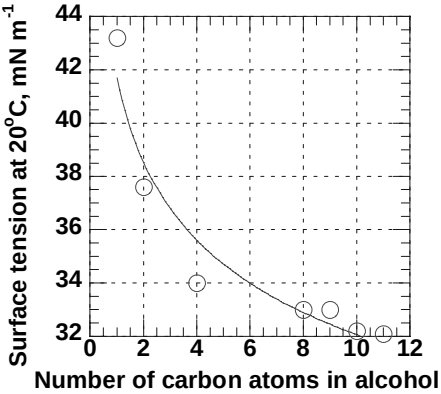


Figure 2.23. Surface tension of esters of phthalic acid and alcohols having different number of carbon atoms.

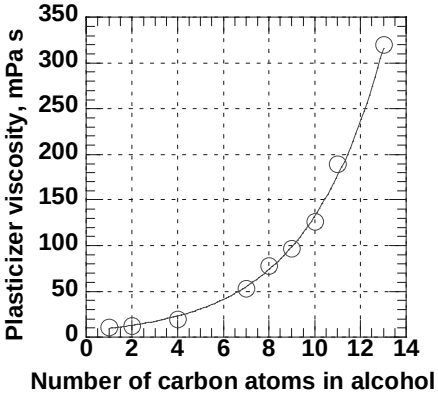


Figure 2.24. Viscosities of esters of phthalic acid and alcohols having different number of carbon atoms.

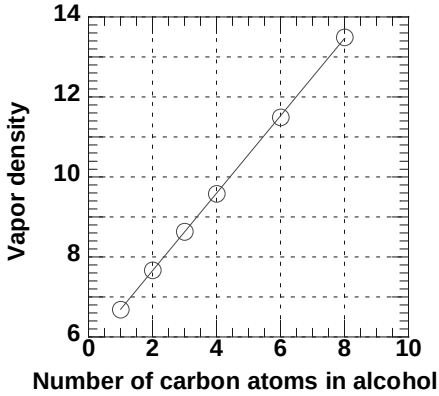


Figure 2.25. Vapor densities of esters of phthalic acid with alcohols having different number of carbon atoms.

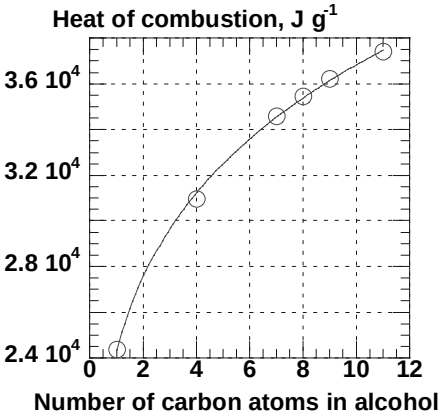


Figure 2.26. Heats of combustion of esters of phthalic acid and alcohols having different number of carbon atoms.

Dielectric constant (Figure 2.19), refractive index (Figure 2.20), specific gravity (Figure 2.21), Hildebrand solubility parameter (2.22), and surface tension (Figure 2.23) all decrease when number of carbon atoms increases.

Viscosity of plasticizer (Figure 2.24) and plastisol, vapor density (Figure 2.25), heat of combustion (Figure 2.26), the theoretical oxygen demand (Figure 2.27), and partition coefficient (Figure 2.28) all increase when the number of carbon atoms in alcohol of plasticizer increases.

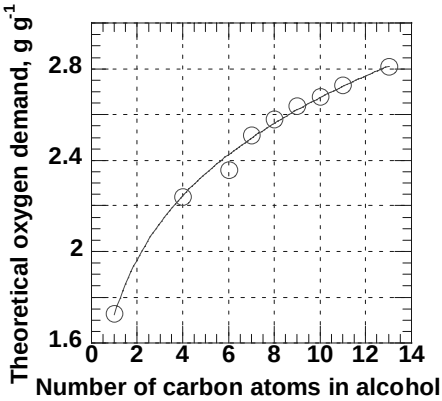


Figure 2.27. Theoretical oxygen demand calculated for esters of phthalic acid and alcohols having different number of carbon atoms.

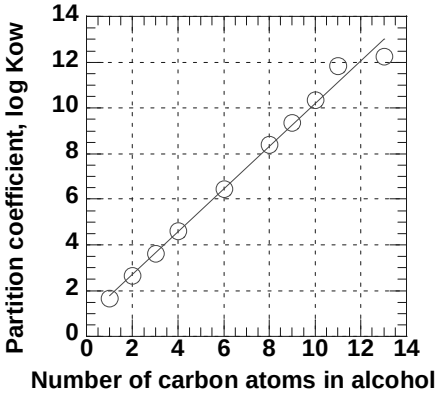


Figure 2.28. Partition coefficients of esters of phthalic acid and alcohols having different number of carbon atoms.

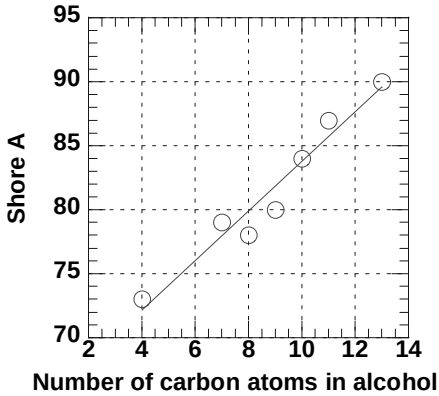


Figure 2.29. Shore A hardness of PVC plasticized with 50 phr of esters of phthalic acid and alcohols having different number of carbon atoms.

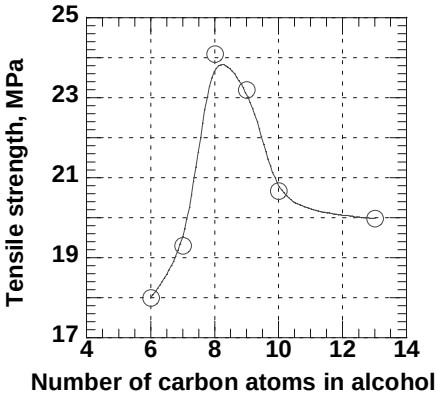


Figure 2.30. Tensile strength of PVC plasticized with 50 phr of esters of phthalic acid and alcohols having different number of carbon atoms.

Figures 2.29-2.31 show the mechanical performance of plasticized PVC containing 50 phr plasticizers of different lengths of their alcohol parts. The data come from technical literature available from the manufacturers literature. Figure 2.29 shows that Shore A linearly increases with the length of carbon atom chain in alcohol part of plasticizer. This data are in agreement with findings presented in Figure 10.2 for sebacates which shows that tensile strength decreases when number of carbon atoms in alcohol part of plasticizer increases. These data also follow simple models of plasticization mechanisms such as gel and lubricity theories but do not seem to account for compatibility between the plasticizer

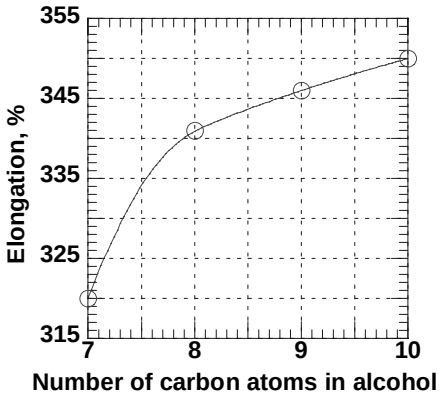


Figure 2.31. Elongation of PVC plasticized with 50 phr of esters of phthalic acid and alcohols having different number of carbon atoms.

and the polymer as shown in Figure 2.22. The data on Shore A show that with the decrease in the number of active molecules of plasticizer (or increase in their molecular weight) hardness of material increases as suggested by the above mentioned theories. Figure 2.30 shows that the tensile strength increases until the plasticizer reaches eight carbon atoms in alcohol, to decrease gradually for a larger number of carbon atoms. In its left section of the curve, the data agree with the Shore A data. The right part of the curve may be due to determination error, influence of compatibility (Hildebrand solubility parameter for PVC is 19.6 $(MPa)^{1/2}$ which in Figure 2.22 is similar to dibutyl phthalate with difference gradually increasing for higher alcohols). The right part of the curve in Figure 2.30 may also be explained by assuming that longer plasticizers have larger molecules than the supposedly helical structure of PVC unit and this interferes with the material's morphology and affects mechanical properties. Finally, Figure 2.31 shows that elongation increases with increase in the length of carbon chain of alcohol. This data does not conform with the gel and lubricity theories (less molecules are available with higher alcohols if plasticizer is used at the same weight proportion to PVC (50 phr) and thus elongation should decrease). On the other hand, the elongation data can be explained by the Moorshead theory (see Section 5.1.3 and Figure 5.3). With a longer alcohol part, a plasticizer can isolate more carbons in a PVC chain and thus make it more flexible.

This discussion shows that our knowledge of plasticizers is far from complete. Even for well-studied plasticizers such as phthalates, simple data from mechanical testing cannot be explained without ambiguity. Not only that data cannot be explained but theories conflict with each other.

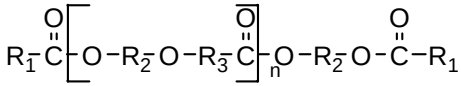
Efforts to recover plasticizers or their main structural units are reported in literature.[94,106] In one potential solution, transesterification of terephthalate polyester scrap was proposed.[106] This results in degradative synthesis of terephthalate plasticizer. In another development, PVC containing phthalates are exposed to catalyzed cracking process in which phthalic anhydride is produced and isolated.[94] Many processes of synthesis of phthalates and their substrates are known from patent literature[95-105] and these are discussed in Section 2.3.

2.2.18 POLYMERIC PLASTICIZERS

2.2.18.1 Esters

The following chemical formulas describe general structure of polyester plasticizers:

Acid terminated-polyester

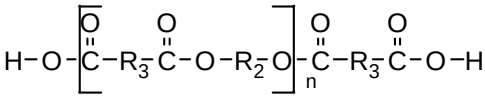


R_1 = mono- or di-carboxylic acid rest

R_2 = glycol rest

R_3 = dicarboxylic acid rest (R_3 may be the same as R_1)

Hydroxyl-terminated polyester



R_2, R_3 see above

These structures show that three generic types are produced:

- polyester produced with excess of dicarboxylic acid
- polyester produced with excess of glycol
- polyester terminated by addition of monocarboxylic acid (e.g., lauric)

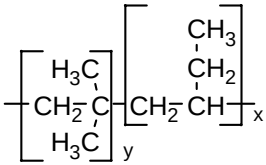
Typical components of these plasticizers are given in the table based on the manufacturer's literature and other sources.[107-114]

Property	Value		
	minimum	maximum	median
Main glycols used in commercial products	1,3-butanediol, 1,4-cyclohexanedimethanol,[107] 2-methylpropane-1,3 diol,[109] neopentyl glycol, 1,2-propanediol,[109]		
Main acids used in commercial products	adipic, azelaic, fatty acids, glutaric, mixed dibasic, phthalic, sebacic, succinic[108]		
Molecular weight, daltons	900	6,400	4,200
NFPA health	1	2	1
NFPA flammability	1	2	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, NBR, PVC-PVA copolymers, acrylics, natural & synthetic rubber, CAB, CN, EC, PVB, chlorinated rubber, nitrocelulose		
Main fields of application	automotive parts, flooring, decorative decals, tank liners, refrigerator gaskets, footwear, adhesives, sealants, coatings, cables, wires, lacquers, print rolls, hose, seals, belts, o-rings, vinyl tapes, electrical insulation, upholstery		

Property	Value		
	minimum	**maximum**	**median**
Outstanding property	migration and extraction resistance, weather stability (some)		
Freezing point, ^{o}C	7	-29	-9
Boiling point, ^{o}C	>315.6	398.9	
Flash point, ^{o}C	176.7	315	270
Refractive index at 25°C	1.458	1.514	1.476
Specific gravity at 25°C	1.03	1.21	1.11
Vapor density	20	25	
Vapor pressure at 100°C, kPa	$1.3x10^{-7}$	$1.3x10^{-1}$	
Saponification value, mg KOH/g	445	540	480
Hydroxyl number, mg KOH/g	2	132	20
Moisture content, wt%	0.05	0.13	
Solubility in water at 25°C, wt%	<0.1	0.4	
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	9.19	10.92	9.34
Viscosity at 25°C, mPa s	900	26,500	4,000
Dielectric constant	5.40	8.9	6.13
Surface tension at 20°C, mN/m	35.1	43.0	41.0
Heat of combustion, kJ/kg			28,595
Specific heat at 20°C, kJ/kg K			1.75
Plasticizer's loss (24 h at 87°C), wt%	0.8	2.1	1.1
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	3,500	35,000	14,000
Theoretical oxygen demand, g/g			2.0
Partition coefficient, log Kow			>8.0
Tensile strength, 50 phr, MPa	19.4	20.95	
Elongation, 50 phr, %	310	360	
Shore A hardness, 50 phr	72	86	80
Brittle temperature, 50 phr, ^{o}C	-8	-25	

2.2.18.2 Polybutenes

The following formula characterizes the chemical structure of polybutenes:

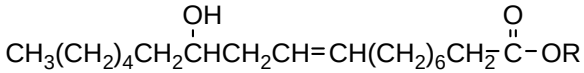


which are copolymers of *y* parts of isoprene and *x* parts of isobutylene.[115-117]

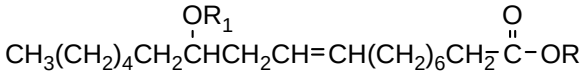
Property	Value		
	minimum	**maximum**	**median**
Main monomers used in commercial products	isoprene, isobutylene, n-butene, methyl vinylidene		
Molecular weight, daltons	180	6,000	910
NFPA health	0	0	0
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PE, PP, PS, ester gums, indene resins, natural rubber, SBR, polyterpene		
Main fields of application	sealants, sealants for double glazed window systems, adhesives, coatings, films, cables		
Outstanding property	low moisture vapor transmission, adhesion		
Freezing point, ^oC	18	-51	-9
Flash point, ^oC	138	193	
Refractive index 20^oC	1.445	1.508	1.47
Specific gravity at 15.5^oC	0.788	0.993	0.83
Vapor pressure at 100^oC, kPa			0.4
Hildebrand solubility parameter, $(cal/cc)^{0.5}$			8.05
Viscosity at 20^oC, cSt	3.5	26,000	400
Volume resistivity, Ohm cm			$1x10^{15}$
Dielectric constant	2.16	2.19	2.18
Specific heat at 40^oC, kJ/kg K	1.84	2.3	2.05
Thermal conductivity at 40^oC, W/m K	0.112	0.118	0.114
Plasticizer's loss (24 h at 87^oC), wt%	0.2	2.0	
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg			>34,600
Theoretical oxygen demand, g/g			3.42

2.2.19 RICINOLEATES

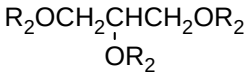
Three structures may be associated with ricinoleates:



R = methyl, ethyl, butyl



R = butyl, R_1 = acetyl



R_2 = ricinoleic acid rest

These plasticizers are seldom used because double bonds in ricinoleic acid are easily oxidized. The last formula is characteristic of castor oil which contains 89% of ricinoleic acid. This group of plasticizers has a historical value since ricinoleates were used as early plasticizers in PVC and cellulosics.

Property	**Value**		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	butanol, ethanol, methanol		
Molecular weight, daltons	321.5	932	396
NFPA health	0	2	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Fields of potential application	textile finishing, caulks, coated fabrics, oil-based paints, varnishes, cosmetics		
Outstanding property	oxidation		
Freezing point, ^oC	-12	-30	
Flash point, ^oC	190	282	
Refractive index	1.458	1.473	1.462
Specific gravity	0.925	0.965	0.945
Solubility in water at 25^oC, wt%			<0.1
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.47	8.58	8.52
Dielectric constant	4.37	5.02	4.89
Surface tension at 20^oC, mN/m	35.2	39.0	
Plasticizer's loss (24 h at 87^oC), wt%	7.0	16.0	12.1

Property	Value		
	minimum	maximum	median
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
Partition coefficient, log Kow	6.48	8.96	
Shore A hardness, 50 phr	68	80	75
Clash-Berg temperature, 50 phr, ^{o}C	-43	-65	-54

2.2.20 SEBACATES

The chemical structure of sebacates is given in the following formula:

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2(CH_2)_6CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OR$$

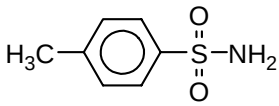
R = alcohol rest (see table below)

Property	Value		
	minimum	maximum	median
Main alcohols used in commercial products	butoxyethanol, butyl, 2-ethylhexyl		
Molecular weight, daltons	314.5	426.7	402.6
NFPA health	1	1	
NFPA flammability	0	1	
NFPA reactivity	0	0	
Highly recommended for these polymers	PVC, PVDC, acrylics, EC, CN, PMMA, PVAc, PVB, nitrile rubber, neoprene rubber, chlorinated rubber		
Main fields of application	frost-resisting cables, aircraft & car interior, flooring, films, paints, food wrap, pharmaceutical coatings, packaging materials, medical, synthetic leather		
Outstanding property	excellent low temperature flexibility		
Freezing point, ^{o}C	-10	-67	
Boiling point, ^{o}C			345
Flash point, ^{o}C	185	224	204
Refractive index at 25°C	1.441	1.483	1.452
Specific gravity at 25°C	0.912	0.971	0.936
Vapor density			10.8
Vapor pressure at 20°C, kPa			4.6×10^{-4}
Moisture content, wt%	0.02	0.05	
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.34	8.68	8.45
Viscosity at 20°C, mPa s	8	25	

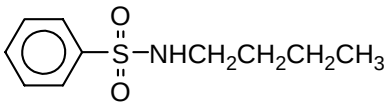
Property	Value		
	minimum	maximum	median
Dielectric constant	2.34	4.63	3.89
Surface tension at 20°C, mN/m			32
Heat of vaporization at 25°C, J/g	225	295	259
Plasticizer's loss (24 h at 87°C), wt%			4.2
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg			1280
Theoretical oxygen demand, g/g	2.34	2.73	2.49
Partition coefficient, log Kow	5.75	10.08	6.30
Tensile strength, 50 phr, MPa			18.5
Elongation, 50 phr, %			240
Shore A hardness, 50 phr			73
Clash-Berg temperature, 50 phr, °C	-50	-69	

2.2.21 SULFONAMIDES

The following chemical structures are representative of sulfonamide plasticizers:



p-toluenesulfonamide



N-butylbenzenesulfonamide

The compound on the left is solid at room temperature (melting point of 137.5°C). The compound on the right is liquid (melting point -30°C). This shows the main direction of influence of chemical structure on the properties of the plasticizer.

Property	Value		
	minimum	maximum	median
Molecular weight, daltons	171.2	256.5	213.3
NFPA health	1	2	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PA6, PA11, PA12, PC, copolyester, melamine, urea, phenolic		
Main fields of application	medical devices, films, fishing lines, automotive		
Outstanding property	improvement of electric conductivity,[120] improvement of fatigue resistance,[122] reduction of melt flow with no effect on impact strength,[123] non-fogging[124]		

Property	Value		
	minimum	**maximum**	**median**
Freezing point, ^oC	137.5	-30	
Boiling point, ^oC	314	350	340
Flash point, ^oC	174	216	202
Refractive index at 20^oC	1.524	1.540	1.530
Specific gravity	1.146	1.18	
Vapor pressure at 140^oC, kPa			$4.66x10^{-2}$
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	12.68	16.22	14.39
Viscosity at 20^oC, mPa s	150	180	
Dielectric constant			3.51
Surface tension at 20^oC, mN/m			44.5
Heat of vaporization at 25^oC, J/g	461	564	510
Specific heat at 20^oC, kJ/kg K			1.92
Plasticizer's loss (24 h at 87^oC), wt%	6.2	33.2	
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	1725	2050	
Theoretical oxygen demand, g/g	2.05	2.43	2.32
Partition coefficient, log Kow	0.92	3.65	2.31
Shore A hardness, 50 phr	86	100	

Sulfonamide plasticizers have unusually high solubility parameters.[119] They are not compatible with PVC. PVC plasticized with sulfonamides experience high loss of plasticizer (see the above table), but sulfonamides are compatible with many other polymers which also have high values of solubility parameters, such as the polymers listed in the above table.

The electrically conductive blends are made from a mixture of PVC and polyaniline.[120] In order to increase conductivity of such blends a plasticizer is typically added to the formulation. Phthalates are compatible with PVC because their solubility parameters are fairly close. Polyaniline has a high solubility parameter as do sulfonamide plasticizers. Figure 2.32 shows mixtures of polyaniline and PVC containing different proportions of both polymers.[120] Conductivity increases with an increase in the amount of polyaniline but this increase is faster in the presence of sulfonamide plasticizer. To increase conductivity, the mobility of polyaniline, which is a conductor, must be increased by the addition of a plasticizer. This is more efficiently done by a sulfonamide plasticizer because it is more polar and comparable in polarity with polyaniline.

Polyamides are another group of highly polar polymers which are successfully plasticized with sulfonamides. Sulfonamides and polyamides have similar ranges of solubility parameters. Figure 2.33 shows the effect of addition of N-butyl benzene sulfonamide on fatigue resistance of monofilaments.[122]

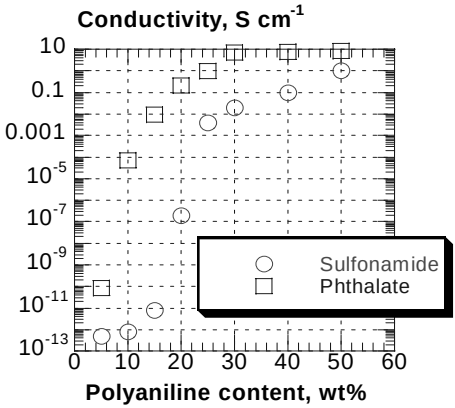


Figure 2.32. Effect of polyaniline content in PVC/ polyaniline blend and plasticizer type on conductivity. [Data from Kulkarni V G, Wessling B, **US Patent** 5,217,649, 1993.]

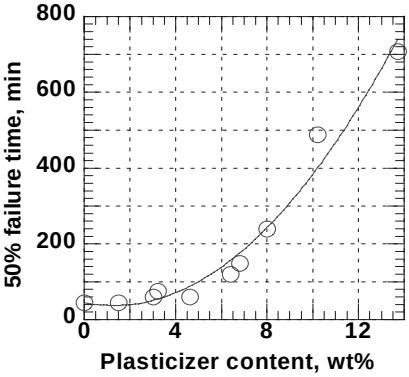


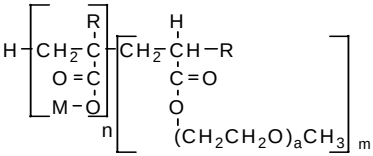
Figure 2.33.Fatigue resistance of polyamide monofilaments vs. sulfonamide plasticizer content. [Data from Wang T-C, **US Patent** 6,249,928, 2001.]

Very small additions of sulfonamide plasticizer (0.25 to 2 phr) were used with polycarbonate.[123] Melt flow index doubles with addition of 0.3 to 0.5 phr depending on sulfonamide chemical composition. At the same time, this small addition does not affect impact strength.

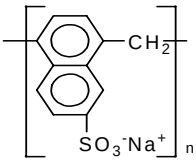
Sulfonamide plasticizers were successfully applied in the production of non-fogging automotive adhesives based on polyurethane and ethylene vinyl acetate copolymer.[124]

2.2.22 SUPERPLASTICIZERS AND PLASTICIZERS FOR CONCRETE

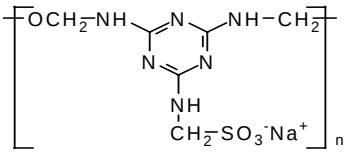
Information on plasticizers and superplasticizers is included in Section 13.5. The following are the structures of some commercially used superplasticizers (chemical compositions of plasticizers are listed in Section 13.5):[125-129]



R= H or methyl; M=metal
acrylic acid-based polycarboxylate



β-naphthalene sulfonate



polymelamine sulfonate

Superplasticizers were discovered in 1960s. The poly-β-naphthalene sulfonates were the first to be introduced and the most widespread superplasticizers followed by polymelamine sulfonates.[126] Organic polymers having carboxylic group are the most recent

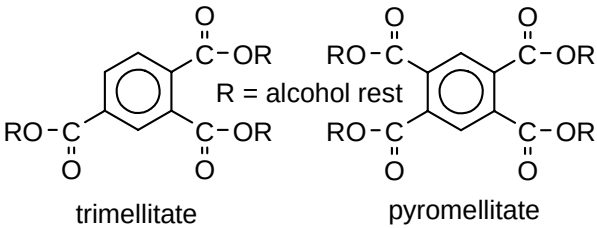
additions to the product range and they form so-called comb-type superplasticizers which maintain fluidity of concrete for a longer period of time without causing extensive retardation of cure. Important properties of plasticizers and superplasticizers used in concrete are very different from requirements of other plasticizers discussed in this book. In many cases very little information is given by manufacturers about physical properties of their products. For these reasons, only limited information is given in the table below.

Property	**Value**		
	minimum	**maximum**	**median**
Molecular weight, daltons	23,000	28,000	
NFPA health	1	2	1
NFPA flammability	0	1	1
NFPA reactivity	0	0	0
Main fields of application	concrete industry		
Outstanding property	reduction of water required, improved slump resistance		
Freezing point, ^{o}C	-5	0	
Boiling point, ^{o}C		105	
Flash point, ^{o}C	93		
Specific gravity	0.8	1.26	
Vapor pressure at 25°C, kPa			3.2
Solubility in water at 25°C, wt%		100	
Viscosity at 20°C, mPa s		128	
TLV-TWA 8 h, OSHA, mg/m^3	2.5	18	
LD50, acute - rat oral, mg/kg	710	1260	

Figure 2.34 shows that the amount of water required decreases linearly with the increase in the amount of added superplasticizer. Figure 2.35 shows that the Marsh flow time decreases with the increase in the amount of superplasticizer. Decrease in the Marsh flow time is initially very rapid but eventually it levels off.

2.2.23 TRI- AND PYROMELLITATES

The following chemical structures characterize tri- and pyromellitates. The most common alcohols used in commercial products are listed in the table below.[130-134]



Property	Value		
	minimum	**maximum**	**median**
Main alcohols used in commercial products	2-ethylhexyl, 2-propenyl, C_7 to C_9, C_8 to C_{10}, nonyl		
Molecular weight, daltons	330.34	630	546.79
NFPA health	1	2	1
NFPA flammability	1	1	1
NFPA reactivity	0	0	0
Highly recommended for these polymers	PVC, PS,CN, CA, CAB, EC, PMMA, rubber		
Main fields of application	cable & wire, sheet, film, interior automotive, medical tubing, blood bags, gaskets, profiles, anti-fogging coatings, upholstery, artificial leather, adhesives, tapes		
Outstanding property	low volatility and migration, heat and UV resistance, electric insulation		
Freezing point, ^oC	-30	-56	-38
Boiling point, ^oC	414	430	
Flash point, ^oC	246	265.6	250
Refractive index	1.480	1.487	1.485
Specific gravity at 20^oC	0.9733	0.994	0.984
Vapor density			18.9
Vapor pressure at 20^oC, kPa	$9.3x10^{-8}$	$6.0x10^{-3}$	
Moisture content, wt%	0.03	0.1	
Solubility in water at 25^oC, wt%	0.001	0.0001	
Hildebrand solubility parameter, $(cal/cc)^{0.5}$	8.75	9.00	
Viscosity at 20^oC, mPa s	124	320	194
Volume resistivity, Ohm cm	$5.0x10^9$	$3.4x10^{13}$	
Dielectric constant	4.23	6.68	4.66
Surface tension at 20^oC, mN/m	33.7	34.9	
Heat of combustion, kJ/kg			34,610
Plasticizer's loss (24 h at 87^oC), wt%	0.3	1.1	0.5
TLV-TWA 8 h, OSHA, mg/m^3	not determined		
NIOSH-IDHL, mg/m^3	not determined		
LD50, acute - rat oral, mg/kg	>3,200	>5,000	
Theoretical oxygen demand, g/g	1.89	2.54	
Partition coefficient, log Kow	4.04	13.09	11.59
Tensile strength, 50 phr, MPa	17.12	27.0	21.45
Elongation, 50 phr, %	302	410	365
Shore A hardness, 50 phr	70	93	72

Property	Value		
	minimum	maximum	median
Clash-Berg temperature, 50 phr, ^{o}C	-28	-44	-32

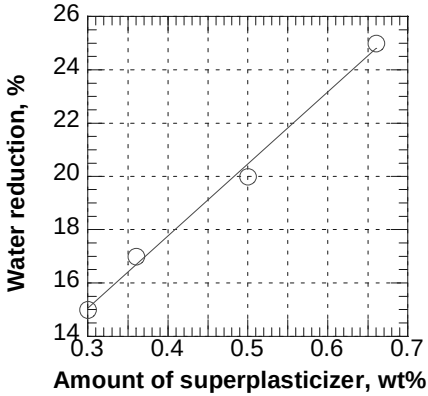


Figure 2.34. Reduction of water required as a function of the amount of W-30 superplasticizer. [Data from W-30 Superplasticizer. Specco Data, January 2000.]

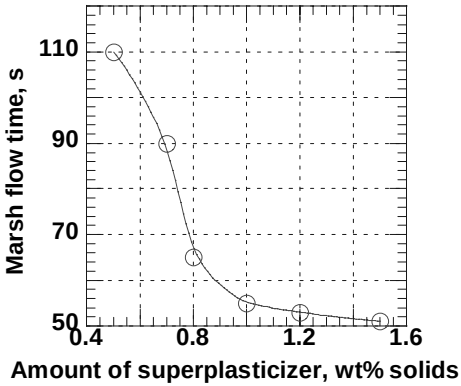


Figure 2.35. Marsh flow time of concrete containing variable amount of superplasticizer.

2.2.24 OTHER PLASTICIZERS

The above groups contain plasticizers which have several representatives of similar chemical structure. There still are plasticizers in common use or that were invented for specific purposes. These can be grouped as follows: biphenyl derivatives,[135-136] calcium stearate,[137] carbon dioxide,[138] difurans,[139,140] fluorine-containing plasticizers,[141] hydroxybenzoic acid esters,[142] isocyanate adducts,[143-149] malonates,[150,151] multi-ring aromatic compounds,[152-155] natural product derivatives,[156-159] nitriles,[160] siloxane-based,[161,162] tar-based products,[163] thioeters,[164] and blends.[165-168] These less frequently used plasticizers are discussed in the above mentioned order.

2.2.24.1 Biphenyl derivatives

Alkylation of biphenyl with cyclohexene gives dicyclohexylbiphenyl, which can be used as a secondary plasticizer for PVC.[135,136] Synthesis of this plasticizer uses Friedel-Crafts reaction with aluminum chloride employed as a catalyst. The application data shows that weight loss and the retention of mechanical properties (tensile strength, elongation, and modulus) are greatly improved with this plasticizer.[135] A mixture of di- and tri-alkyl (usually propyl) biphenyls is used as a plasticizer for polystyrene, butadiene rubber, epoxy resin, and polyurethane.[136]

2.2.24.2 Calcium stearate

Calcium stearate performs many functions in polymers. These include PVC costabilizer, lubricant of many polymers, release agent, etc. Polyamide-6, polyesters, polyethylene flow substantially better in the presence of calcium carbonate. Their mechanical properties

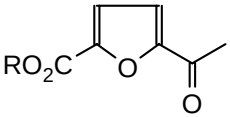
(e.g., impact strength) are also improved, which seems to suggest that calcium stearate plays a role of plasticizer rather than that of lubricant.[137]

2.2.24.3 Carbon dioxide

Many products require a plasticizer to lower viscosity, process temperature, or to increase the rate of flow. In many such products, the plasticizer remaining in the product affects its final properties in a negative way. The use of temporary plasticizers is one possible solution. In practical terms, these are either plasticizers which can be removed after processing or plasticizers that react during processing, forming non-volatile, non-migrating components of a mixture. Supercritical carbon dioxide is one of the examples of the first group of products.[138] Eleven polymers were selected for a study designed to understand relationships between the plasticization pressure of carbon dioxide and the chemical structure of a polymer. No relationship was found with the glass transition temperatures of polymers, their free fractional volume, and the effect of polar groups in the polymer which may interact with carbon dioxide. Instead, it was found that all polymers were plasticized at the same critical carbon dioxide concentration of 36 cm^3 per cm^3 polymer.[138]

2.2.24.4 Difuran diesters

The following chemical formula shows a general structure of difuran plasticizers:[139,140]



R=butyl, hexyl, or 2-ethylhexyl

The above compounds were found to be good plasticizers of PVC. Esters that possess tertiary benzylic-type hydrogen substituents at α position to the furan ring affect color of resin.[139,140]

2.2.24.5 Fluorine-containing plasticizers

Fluoropolymers have many very useful properties but they are difficult or impossible to process by the conventional methods. Processing characteristics can be improved by suitable plasticizers having characteristics that do not affect final properties of products and remain in the plasticized materials under their conditions of performance. Fluoropolymers have very low solubility parameters and are not compatible with conventional plasticizers. Many simple compounds, such as fluorobenzene, chlorofluorinated aromatic hydrocarbons, and fluorinated oils were used as plasticizers but they are not permanent. In the last three decades, oligomers, fluoropolymers, fluorosilicone polymers, fluorinated polyethers were considered as plasticizers of fluoropolymers of high molecular weight. In the most recent invention, high-boiling, highly-fluorinated, polycyclic alkanes having predomi-

nantly perfluorinated aliphatic fused-ring structures are proposed as plasticizers. Their structure is complex. One possible component has the following structure:

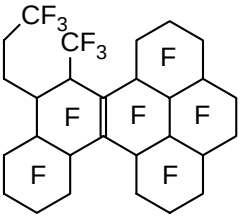
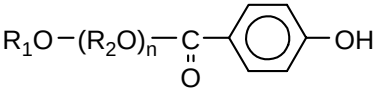


Figure 2.36 shows that addition of this plasticizer to tetrafluoroethylene/perfluoro(alkyl vinyl) ether, TFE/PPVE, increases its melt flow index.[141] Figure 2.37 shows that the addition of plasticizer causes almost linear increase in the tensile strength.[141] This is unusual and it is most likely caused by the modification of crystalline structure and mode of failure. Addition of this plasticizer to polytetrafluoroethylene, PTFE, improves its mechanical performance and processing abilities by sintering.[141]

2.2.24.6 Hydroxybenzoic acid esters

The derivative of p-hydroxybenzoic acid having a following structure:

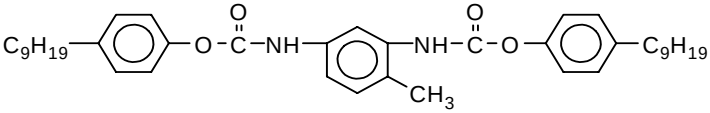


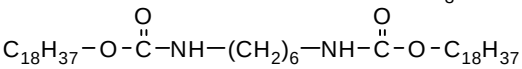
R_1=C_6 TO C_{10} alkyl group
R_2=C_2 to C_4 alkylene group

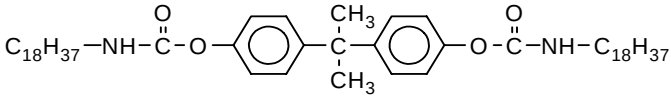
was found to be a good plasticizer of polyamide-11 and polyamide-12. Plasticizer has low volatility. It improves low temperature impact resistance, oil resistance, and flexibility.[142]

2.2.24.7 Isocyanate adducts

Some low molecular adducts are used in plasticization of polycarbonate:







These compounds are added in very small quantities (0.5 to 1 phr) but these small amounts increase melt flow index by up to 60% and slightly improve impact strength.[144]

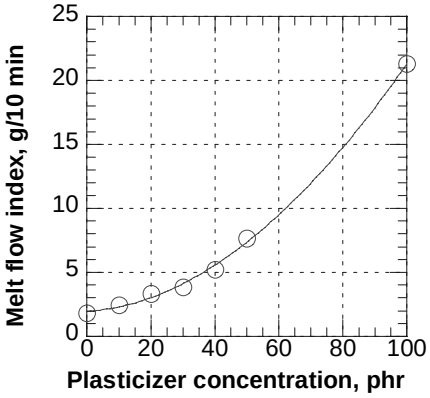


Figure 2.36. Effect of fluoroplasticizer on melt flow index of tetrafluoroethylene/perfluoro(alkyl vinyl) ether. [Data from Steward CH W, Spohn P D, **US Patent** 5,356,986, 1994.]

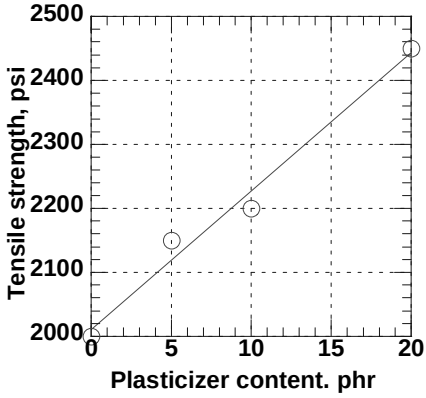
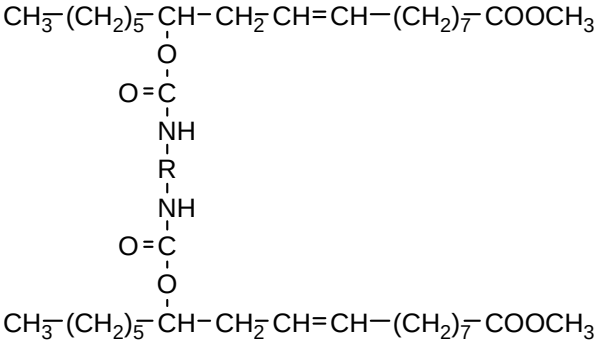


Figure 2.37. Effect of fluoroplasticizer on tensile strength of hydrogen-containing fluoroelastomer. [Data from Steward CH W, Spohn P D, **US Patent** 5,356,986, 1994.]

Derivatives of ricinoleic acid and isocyanate:

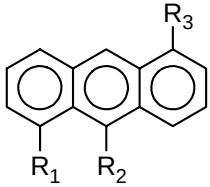


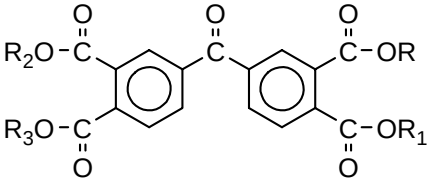
are used as a plasticizer for PVC.[146,148,149] R in the above formula stands for any rest of suitable isocyanate.

Polyurethane-based plasticizers can be obtained as a product of hydrolysis of polyurethane scrap as described elsewhere for material from printing rollers.[143,145] These plasticizers were used to modify acrylonitrile-butadiene rubber.[143,145] In still another development, diurethane was used in polyurethane elastomers.[147] Addition of diurethane improved potlife, and mechanical properties. The plasticizer performed better than DOP and it was substantially less migrating than DOP.[147]

2.2.24.8 Multi-ring aromatic compounds

The following chemical structures characterize some plasticizers obtained from multi-ring aromatic compounds:





R_1, R_2, R_3 = C_3 to C_{12} alkyls R, R_1, R_2, R_3 = C_4 to C_{22} alkyls

alkyl substituted anthracene tetraester of benzophenone-tetracarboxylic acid

Alkyl substituted anthracene has found application in plasticization of poly(N-vinyl carbazole) residing in photoconductive layer of imaging member.[152]

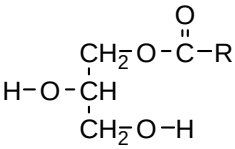
The tetraester of benzophenone-tetracarboxylic acid has found application as non-migrating plasticizer of polyvinylchloride.[153]

A process for making naphthalene hydrodimer mixtures from tetralin or alkyltetralin is available. The resultant mixture was found to be a good PVC plasticizer which may replace part of DOP.[154,155] There is a good compatibility between the plasticizer of an invention and polyvinylchloride and DOP as is evident from the presented data on tensile strength, modulus and elongation.[154,155]

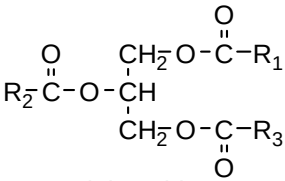
2.2.24.9 Natural product derivatives

Two reasons drive research in this area: hope to find the sustainable resources and the expectation that derivatives of natural products are less toxic and thus suitable in medical, pharmaceutical, and food applications.

Mono- and triglycerides are some examples of plasticizers obtainable from natural products:



mono- and



triglyceride

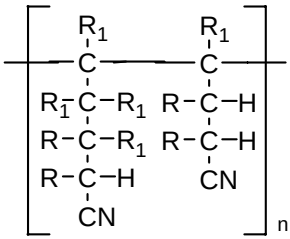
Monoglyceride[157,168] is a commercial product known as Eastman EPZ plasticizer useful in medical, pharmaceutical and food applications of flexible PVC. It is obtained by by interesterification of fully hydrogenated coconut oil and glyceryl triacetate. It is approved for direct and indirect contact with food by FDA.

The triglyceride plasticizer can be composed of aliphatic hydrocarbon groups having 1 to 20 carbon atoms (preferably 5 to 9 carbon atoms).[156] A plasticizer of this invention is suggested for use as hemolysis depressant protecting blood erythrocytes in polyvinylchloride appliances for medical applications.

A biocompatible product may be plasticized by lipids.[158] Lipids were found to be compatible with over 20 different polymeric materials. Vegetable oils were found to be suitable as plasticizers.[159]

2.2.24.10 Nitriles

Dinitrile given by the following formula:

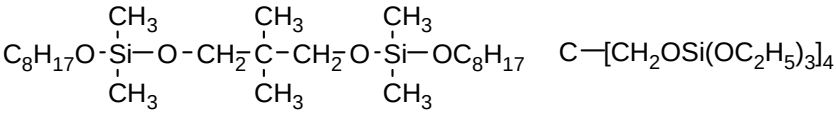


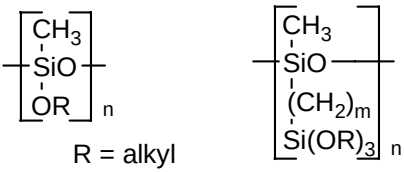
R, R_1 = hydrogen or hydrocarbyl radical

is suggested as a suitable plasticizer for a conjugated diene-unsaturated nitrile rubber.[160] This plasticizer was to be excellent replacement for DOP. Comparison of both plasticizers shows that the same or better mechanical performance and processing characteristics can be obtained.

2.2.24.11 Siloxane-based plasticizers

Siloxanes and polysiloxanes having the following formulas:





R = alkyl

are used in polycarbonates[161] and rubber compositions.[162] Small additions of siloxanes (0.1 to 0.5 phr) increase melt flow index by 50 to 70% without changing impact strength.[161]

Polysiloxane added to tire tread rubber composition improves processing characteristics of rubber containing silica but also improves several characteristics of tire such as temperature dependency of hardness, grip on ice/snow, abrasion resistance, etc. Polysiloxane does not migrate from tire composition.[162]

2.2.24.12 Tar-based products

Tar-based products are used in conjunction with polymers in the manufacture of polymer-reinforced membranes which are biostable and moisture impermeable. In this combination, polymer (polyurethane or some styrene-containing block copolymers) offers reinforcing network but it is also plasticized to produce elastomeric materials having excellent

elongation and shape memory. In these products plasticizers are obtained from tar without special processing. A technology is also discussed that allows to produce a plasticizer by controlled oxidation of tar to produce a pitch suitable for manufacture of graphite products.[163]

2.2.24.13 Thioeters

Chloroprene rubber can be plasticized with a thioether represented by the following formula:

$$R_1(OR)_mS(RO)_nR_2$$

$$R = C_2 \text{ to } C_4 \text{ alkylene group}$$
$$R_1, R_2 = C_4 \text{ to } C_{24} \text{ monoacyl groups}$$

It was demonstrated that this plasticizer has excellent retention and low temperature properties.[164]

2.2.24.14 Blends

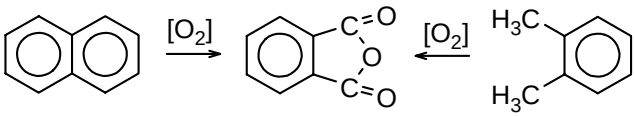
High concentrations of plasticizers have been used in plasticization of polyvinylbutyral used in the architectural glazing interlayers.[165] Compatibility, low temperature flexibility and impact strength are important parameters, which must work in combination for material to perform. It was found that a mixture of phthalates (benzyl and alkyl containing a mixture of C_3 to C_6 alcohols) and alkyl adipates (mixture of C_5 to C_8 alcohols) is useful in this application.[165]

In another invention,[166,167] plasticizers are prepared from a mixture of acids (acrylic, maleic, and fumaric) and alcohols having 6 to 18 carbon atoms. Mono and diesters are obtained during manufacturing process. The composition of stock is controlled to obtain plasticizer which has good electrical insulation properties, water extraction resistance, and fogging resistance.[166,167]

2.3 METHODS OF SYNTHESIS AND THEIR EFFECT ON PROPERTIES OF PLASTICIZERS

Quality of raw materials used for the synthesis of plasticizers has influence on their properties. Well-defined quality of plasticizer is especially important in applications such as food contact, medical, pharmaceutical, and electrical insulation, which frequently require special grades.

Phthalates are obtained from phthalic anhydride. Phthalic anhydride is a product of catalytic oxidation of naphthalene and o-xylene:



The o-xylene route is more frequently used today. Phthalic anhydride can also be recovered from waste plastics containing phthalates.[94] The invention is based on finding that when the phthalate ester is heated, usually not only ester is vaporized but it is also at least partially cracked into phthalic acid and an alcohol component corresponding to an

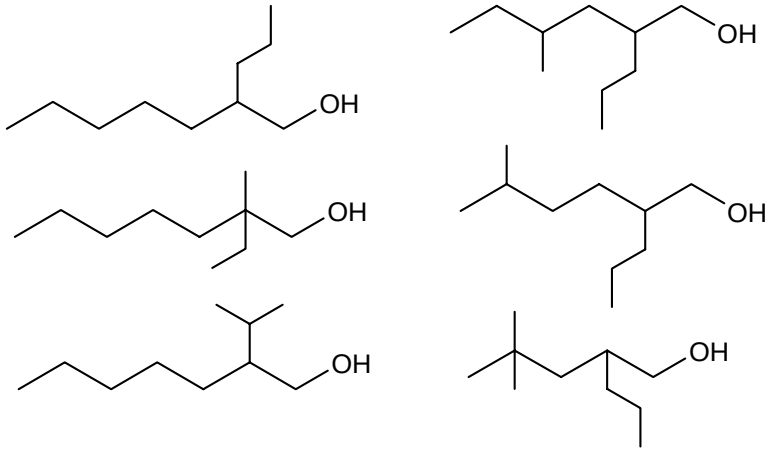
alkyl group of the ester, and also other hydrocarbons such as a dehydrated compound from the alcohol, cracked hydrocarbon from the alcohol and other products are formed. For example, when dioctyl phthalate is heated, octanol and octene may be formed in addition to phthalic acid. Usually, phthalic acid is immediately dehydrated so that phthalic anhydride is produced.[94] The system described in the invention allows to recover not only components of a plasticizer but also hydrogen chloride from PVC and other vital components which can be reused. This creates the possibility of conservation of natural resources by proper use of technology.

Various other processes not discussed here lead to manufacture of acids required for production of plasticizers. As previously mentioned, availability and price of acid may predetermine price and thus the likelihood of a plasticizer's use. Acids are used not only in their pure forms but also in form of mixtures. For example DBE intermediates manufactured by DuPont are refined dimethyl esters of adipic, glutaric, and succinic acid are mixtures for plasticizer synthesis.[108] There are six mixtures of different composition which may be used for the production of polyester and diester plasticizers. Diester plasticizers are produced by transesterification according to the following equation:

$$2ROH + CH_3OC(=O)(CH_2)_nC(=O)OCH_3 \xrightarrow{\text{catalyst}} ROC(=O)(CH_2)_nC(=O)OR + 2CH_3OH$$

The alcohol part comes from various synthetic sources. One source described in literature is C_9 alcohol mixture that is obtained by the hydroformylation and hydrogenation of C_8 olefin mixture obtained by dimerization of butene fraction.[98,100,104] Two processes of purification are used by this technology. First consistent octene fraction obtained by the butene dimerization is purified by distillation. This is followed by rectification of reaction mixture obtained from alcohol production. After the plasticizer is produced it is still purified by usual methods used in plasticizer synthesis.[100]

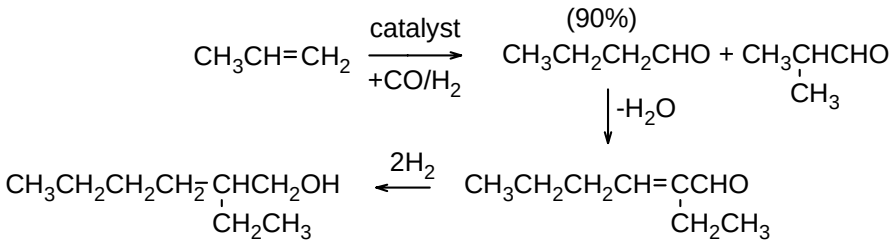
Another invention describes the technology of production of C_{10} alcohol mixture which comprises 2-propylheptanol.[170,171] "Butene fraction" used as a starting material, includes fractions containing butenes as the main component obtained by thermal cracking of hydrocarbon oils including naphtha. C_{10} alcohol mixture can be obtained by subjecting the above-mentioned butene fraction to hydroformylation, aldol condensation, and hydrogenation. The details included in the technological process are not discussed here but an example is given to show potential composition of alcohols produced. The following isomers are produced in this technological process.



The structure at the upper left corner characterizes the main product. The above technology shows that synthesis of these products gives a mixture of several isomers. Process controls and purification methods allow to keep concentrations within the required limits. Decyl alcohols are also obtained by oligomerization of propylene in the presence of deactivated zeolites, separation of olefins containing nine carbon atoms, formylation of mixture to aldehyde, and hydrogenation of aldehydes to corresponding alcohols.[95-97,99]

A synthesis of mixtures of C_6 to C_{12} hydrocarbons, their separation, hydroformylation, and hydrogenation to produce alcohols having different number of carbon atoms is described in the invention.[105] Some fractions of these alcohols are used for a production of plasticizers with the remaining hydrocarbon stock being used as a motor fuel.[105]

The synthesis of the most popular alcohol used in the production of plasticizers is explained by the following chemical reactions:



Three stages are involved here. First propylene undergoes hydroformylation in which n-butyraldehyde is produced with a prevailing yield, n-butyraldehyde undergoes self-condensation to produce 2-ethylhexenal, which, after hydrogenation, produces 2-ehylhexyl alcohol. This is an important part of synthesis leading to products other than alcohol which are of importance in the chemical industry.

Many other processes are used to produce alcohols and their mixtures and these are described further elsewhere.[106]

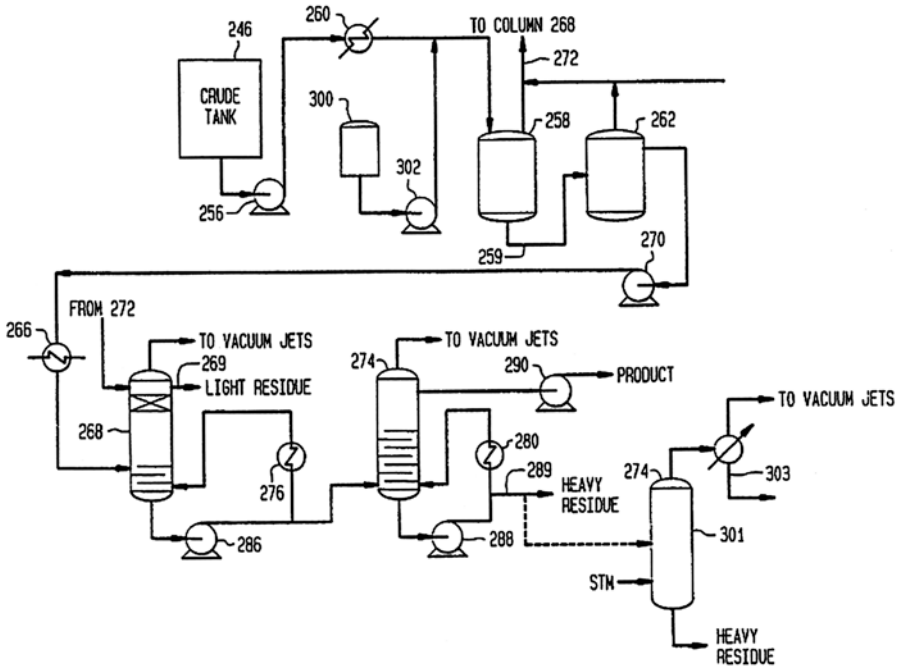


Figure 2.38. Schematic diagram of technological line for purification of phthalic anhydride residue for production of phthalates. [Adapted from Jones L O, Daniels P H, Krauskopf L G, Rigopoulos K R, Schlosberg, **US Patent** 5,534,652, 1996.]

Figure 2.38 shows a stage of the production process of phthalates in which phthalic anhydride residue stream is purified for a production of plasticizers. The crude phthalic anhydride from the oxidation section is stored in tank (246). Tank (246) is heated with steam to maintain the crude phthalic anhydride in a molten state.[172]

Na_2CO_3 can be added to the system in order to treat the crude phthalic anhydride. Na_2CO_3 has a beneficial effect on product quality. A solution of Na_2CO_3 in water can be prepared in drum (300) and meter-pumped upstream of decomposer (258). [172]

The crude phthalic anhydride from tank (246) is heated as it passes through preheater (260) before it enters decomposer vessel (258). The bottoms from decomposer vessel (258) are sent to decomposer vessel (262) *via* conduit (259). Crude phthalic anhydride from decomposer vessel (262) is then pumped through cooler (266) to light ends fractionation column (268) (i.e., first distillation tower) *via* pump (270).[172]

The vapor generated from decomposer vessels (258) and (262) is piped *via* steam-traced conduit (272) directly to the top portion of light ends fractionation column or first distillation tower (268).[172]

The fractionation segment of the finishing section consists of first (topping or light ends) fractionation column or distillation tower (268) and second (tailing or product) fractionation column or distillation tower (274), with their respective reboilers, i.e., column (268) is connected to reboiler (276) and column (274) is connected to reboiler (280). Fully

spared steam jet ejectors (not shown) are also provided on the top of fractionation columns (268) and (274) to provide a column vacuum.[172]

The reboilers are suppressed-vaporization pump-through types with pumps (286) and (288), respectively, which also pump out the bottom products from the associated fractionation column. Finished product from second fractionation column (274) is pumped *via* pump (290) to product tankage, not shown.[172]

The reaction conditions under which esterification occurs can be varied considerably. The reaction proceeds very slowly at room temperature, but quite rapidly at elevated temperatures. About 99% of acids or anhydrides are converted to an ester within a few hours.[173]

To facilitate esterification reaction, it is desirable that water which is formed during esterification, is removed as rapidly as possible. Water has a detrimental effect upon the rate of conversion. Water is removed by carrying out the reaction in a liquid medium which forms an azeotrope having a boiling point that is lower than that of either component of the reaction.[173] In the commercial production of plasticizer esters, such as phthalates, adipates, and trimellitates, conversions of greater than 99% are desired. The unreacted portion of the acid or anhydride will react with the base in the final steps of the esterification process and a water soluble salt will be formed that eventually ends up in a waste treatment stream. Thus, an increased conversion from 99.0% to 99.95% reduces the waste treatment loads associated with treating unconverted acid or anhydride in plasticizer production by a factor of twenty.[173]

The typical process of plasticizer production includes the following steps:[173]

- esterification of an acid or anhydride with excess alcohols and a titanium, zirconium or tin-based catalyst at a temperature and pressure which permits boiling of the mixture in a reactor having a reactor turnover rate in the range between about 2.5 to about 20
- addition of adsorbents such as alumina, silica gel, activated carbon, clay and/or filter aid to the reaction mixture following esterification before further treatment
- addition of water and base to simultaneously neutralize the residual organic acids and hydrolyze the catalyst
- removal of the water used in the hydrolysis step by heat and vacuum in a flash step
- filtration of solids from the ester mixture containing the bulk of the excess alcohol used in the esterification reaction
- removal of excess alcohol by steam stripping or any other distillation method and recycling of the alcohol to the reaction vessel
- removing any residual solids from the stripped ester in a final filtration.

The rate of esterification reaction depends on the temperature of the reaction mixture. This temperature can be affected by order of addition of low boiling component (alcohol). If the entire alcohol needed by reaction stoichiometry is added at once, the reaction temperature decreases and reaction slows down. If only 5% of stoichiometric requirement is added, and the concentration of a free alcohol is maintained throughout the process of esterification, the reaction temperature increases as does the reaction rate.[177]

The quality of the plasticizer can be increased by removal of dissolved oxygen from a feed alcohol.[174] This reduces formation of colored products which reduce quality of the plasticizer or require more rigorous after treatment.

In many methods used to obtain a plasticizer having a high volume resistivity, the treatment is conducted using the adsorbent. A large amount of the adsorbent has to be used and the method becomes uneconomical.[174] A plasticizer ester having an excellent volume resistivity can easily be produced by subjecting an organic acid or its anhydride and an alcohol to an esterification reaction, blowing a carbon dioxide gas into the resulting crude ester to convert the residual alkali into a carbonate, recovering excess alcohol, and then conducting fine filtration using a filter aid.[174]

A process for the titanate catalyzed preparation of plasticizers from polycarboxylic acids and alcohols, which minimizes waste water and is energy efficient, has been patented.[11] The reaction product is treated with aqueous caustic and it is then filtered using an absorbent medium which removes titanium, caustic, acid salts and water. The need for water washing is obviated, and the final plasticizer product has excellent properties. This process can be used for production of phthalates, adipates, and trimellitates.[11]

Production of benzyl butyl phthalate is complicated by the need to use two different substituents. Studies show that many side reactions may take place, that change proportions of three potential phthalates (dibutyl, dibenzyl, benzyl butyl). The proportion of the three components determines properties of the plasticizer. The secondary reactions of hydrolysis leading to formation of unwanted components (dibutyl and dibenzyl) were found to be at a minimum when pH of reaction medium was slightly basic.[175,176]

Mono- and diesters of 2,2,4-trimethyl-1,3-pentanediol and benzoic acid are obtained with a high yield by a process of transesterification in the presence of catalytic amount of base.[21] These plasticizers are useful in stain resistant flooring.

Organic titanates are used as catalysts in the synthesis of citric acid esters.[37] The production steps for the citric acid esters include low temperature esterification at 140°C or below, removal of any excess alcohol and thereafter, alkoxylation. Conventional neutralization and finishing steps are then carried out. The alkoxylation step is carried out at a temperature less than approximately 110°C.[37]

Methods of synthesis of polymeric plasticizers are discussed in several patents.[107,109,110,112] Endcapped polyalkylene ethers were prepared for use in polyester resins.[107] Different propanediol derivatives are synthesized to form polyester-type plasticizer.[109] In the synthesis of polyester-type plasticizer it is important to avoid presence of unreacted acids.[109] A second stage reaction is conducted in order to remove the odor from the polyester plasticizer.[110] First, the plasticizer is synthesized in the presence of a molar excess of alcohol, then hydroxyl groups are reacted with mono- or difunctional isocyanates.[110] Polyester plasticizer is also produced from a waste stream of non-volatiles recovered as a by-product of oxidation of cyclohexanone.

Triaryl phosphates are prepared by phosphorylation of alkyl phenols without phosphorylation catalyst.[82] This simplifies purification of the plasticizer by eliminating the need to withdraw the purified product as a distillate.[82] Mixed alkyl diaryl esters are produced in the presence of a catalytic amount of an alkali metal phenoxide. The plasticizer needs to be separated by distillation.[83] Figure 2.39 shows the distillation process of purification of triaryl phosphates. A crude triaryl phosphate ester reaction mixture is passed

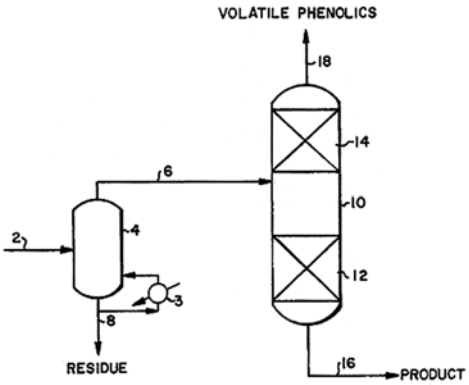


Figure 2.39. Purification process of triaryl phosphate esters. [Adapted from Aal R A, Chen N H C, Chapman J K, **US Patent** 3,945,891, 1976.]

through line (2) into flash distiller (4) operated with a reboiler (3) at a temperature of about 220 to 320°C at about 2 to 10 mm Hg. Catalyst residues and other high boiling impurities are removed as an underflow through line (8) from distiller (4). The catalyst residues are not passed to fractional distillation column (10) in order to reduce catalytic decomposition reactions which result in the formation of increased amounts of phenols. An overhead stream principally containing unreacted free phenol and the desired triaryl phosphate ester product is removed through line (6) and passed to fractional distillation column (10), entering the column midpoint or above in order to promote stripping. Fractional distillation of the unreacted free phenol and the desired triaryl phosphate ester product is carried out in fractional distillation column (10). Fractional distillation is carried out at 250 to 300°C and at a pressure of 4 to 10 mm Hg at column base (12) while column top (14) is at a temperature of 60 to 200°C and at a pressure of 2 to 4 mm Hg. Precise maintenance of temperature and pressure conditions is required to produce a triaryl phosphate ester product having a free phenolic content of 100 ppm or less without the need for an after-treatment process. The product is removed from column (10) as a liquid underflow through line (16). Volatile phenolics pass through column (10) in the vapor state and are removed through overhead line (18). Removal of the triaryl phosphate ester product as a sidestream rather than as a liquid underflow would result in a product having a substantial amount of phenolic contaminants.[88] Phosphate esters are contacted with stannous fatty acid salt to decolorize esters and stabilize then against color formation.[90]

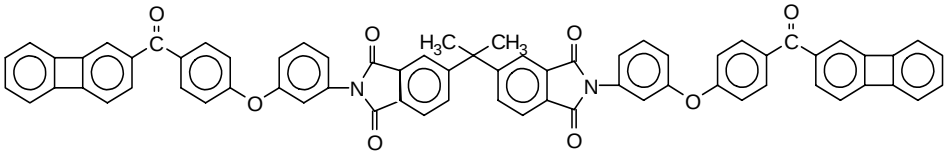
2.4 REACTIVE PLASTICIZERS AND INTERNAL PLASTICIZATION

Some examples of reactive plasticizers,[111,162,178-183] internal plasticization,[184-187] and polymer modification[188-191] are given to show other possibilities of plasticization, which are outside the scope of this monograph.

Reactive plasticizers give three major advantages in formulated product applications:

- addition of low molecular weight material improves processing
- reaction of plasticizer after processing eliminates problems with their migration and volatilization
- polymer properties may be enhanced by chemical reactions.

In polyimide used for high temperature applications a plasticizer having very unusual structure is used:[178]



At an elevated temperature, four membered ring undergoes scission and crosslinks polymer.

Unsaturated trimethylopropane trimethylacrylate is a reactive plasticizer of PVC. Its reaction is initiated by addition of peroxide. Because of crosslinking, PVC material has increased resistance to creep at elevated temperatures.[179]

4,4'-bis(3-ethynylphenoxy)diphenyl sulfone is fluid at room temperature and acts as a plasticizer during early stages of processing thermoplastic polysulfone and then it polymerizes to a rigid resin.[180] Monohydroxy-terminated polybutadiene is a reactive or internal plasticizer for polyurethanes.[181] Polysiloxanes of different chemical structure are used as reactive plasticizers in rubber composition for tire tread.[162] photopolymerizable compounds include components which act as process plasticizers.[183] Polyester contains ethylenically unsaturated terminal groups as does the plasticizer. Groups are reacted after forming an operation to produce a flexible polymer.[111] A monomer is included in a coating composition that polymerizes after processing, which gives elastic coating having no volatile components as do majority of similar coatings.[184]

Comonomer having hexyl side chain was added to N-vinylpyrrolidone to improve its properties.[186] It was found that the inclusion of comonomer reduces glass transition temperature of copolymer because it acts as an internal plasticizer. Polyimides are internally plasticized with alkyl 3,5-diaminobenzoate compounds.[187] Without internal plasticization a polymer has too high a glass transition temperature that makes processing very difficult.

Acrylonitrile-butadiene rubber, NBR, styrene-acrylonitrile rubber, SAN, ethylene-vinyl acetate copolymer, EVA, and acrylic copolymers are helpful modifications of polyvinylchloride that change its processing characteristics and elastomeric properties.[188] Blending with these copolymers helps to reduce the requirement for low molecular weight plasticizers. Ethylene-vinyl acetate copolymer plays a role of high molecular weight plasticizer in production of vinyl hose. This reduces the amount of DOP used in flexible hose applications. Ethylene copolymer is used plasticize PVC that reduces gel.[190] Phthalate plasticizers can be eliminated from water based adhesives because of utilization of vinyl acetate ethylene copolymer as a high molecular plasticizer/modifier.[191]

REFERENCES

1 Kattas L N, Gastrock F, The Individual Additives - Dynamics of Change. Retec 2000.
2 Menzel B, *Kunststoffe*, **86**, 7, p. 992-996, 1996.
3 Kirillovich V I, *Intl. Polym. Sci. Technol.*, **25**, 4, T11-T13, 1998.
4 Gain B, Walsh K, *Chem. Week*, October 1, 1997, p. 28-30.
5 *Plast. Additives Compounding*, October, 1999, p. 12-17.
6 **Plastics Additives in Europe**, *Business Communications, Co.*, January 2002.
7 Markets. European plastics additives, *Additives for Polymers, Elsevier*, January 2002.
8 Phthalic Anhydride. *Eur. Chem. News*, 6-12 Sept. 1999, p. 18.

9 Vames S, *Chem. Week*, May 20, 1998, p. 33-36.
10 Wypych A, **Plasticizers Database**, *ChemTec Publishing*, Toronto, 2004.
11 **US Patent** 5,434,294, 1995.
12 Mirci L E, *Mater. Plast*., **33**, No.4, 1996, p.253-9.
13 Mirci L E, *Mater. Plast*., **33**, No.3, 1996, p.160-7.
14 Mirci L E, *Mater. Plast*., **32**, No.2, 1995, p.96-101.
15 Sears J K, Darby J R, **The Technology of Plasticizers**, *John Wiley & Sons*, New York 1982.
16 Bohnert T, Stanhope B, Gruszecki K, Pitman S, Elsworth V, *J. Vinyl Additive Technol*., **6**, 3, p. 146-149, 2000.
17 Bohnert T; Stanhope B; Gruszecki K; Pitman S; Elsworth V, Antec, Orlando, Fl., 7th-11th May, 2000, paper 648.
18 Lang J; Arendt W D, Versatile Benzoate Blends for Polyvinyl Chloride Applications, Vinyltec '98. Retec proceedings, SPE, Vinyl Div., East Brunswick, N.J., 13th-14th Oct.1998, p.111-20.
19 Arendt W D; Jianmin Lang, *J. Vinyl Additive Technol*., **4**, No.3, Sept.1998, p.184-8.
20 **US Patent** 5,728,760, 1998.
21 **US Patent** 5,153,342, 1992.
22 **US Patent** 5,039,728, 1991.
23 **US Patent** 5,006,585, 1991.
24 Environment Health Criteria 181. Chlorinated Paraffins. United Nations Environment Programme. World Health Organization, Geneva, 1996.
25 Canadian Environmental Protection Act. Priority Substances List. Assessment Report. Chlorinated Paraffins. Environment Canada, En 40-215/17E.
26 Tomy G T; Westmore J B; Stern G A; Muir D C G; Fisk A T, *Analytical Chem*., **71**, No.2, 15th Jan.1999, p.446-51.
27 Vecera M, *Pitture Vernici*, 1995, 11, p.14-20.
28 **US Patent** 4,022,812, 1977.
29 Paroil Liquid Chlorinated Paraffins, Dover Chemical Corporation.
30 Jain K K; Fatma K; Saroop M, *Popular Plast. Packaging*, **43**, No.11, Nov.1998, p.75/82.
31 **US Patent** 6,534,577, 2003.
32 **US Patent** 5,227,155, 1993.
33 **US Patent** 5,225,185, 1993.
34 **US Patent** 5,145,671, 1992.
35 **US Patent** 5,145,670, 1992.
36 **US Patent** 5,066,484, 1991.
37 **US Patent** 4,931,583, 1990.
38 **US Patent** 4,892,967, 1990.
39 **US Patent** 4,870,204, 1989.
40 **US Patent** 4,824,893, 1989.
41 **US Patent** 4,789,700, 1988.
42 **US Patent** 4,711,922, 1987.
43 Adams R C, *Medical Plast Biomater.*, 2001.
44 Diltiazem HCl Sustained release Pellets, Degussa, Feb. 2002.
45 **US Patent** 5,380,777, 1995.
46 **US Patent** 6,592,692, 2003.
47 **US Patent** 6,425,966, 2002.
48 **US Patent** 5,783,769, 1998.
49 **US Patent** 5,532,390, 1996.
50 **US Patent** 5,458,706, 1995.
51 **US Patent** 5,310,433, 1994.
52 **US Patent** 5,220,039, 1993.
53 **US Patent** 5,205,983, 1993.
54 **US Patent** 5,124,463, 1992.
55 **US Patent** 4,997,499, 1991.
56 **US Patent** 4,711,679, 1987.
57 **US Patent** 4,482,411, 1984.
58 **US Patent** 4,482,410, 1984.
59 **US Patent** 4,482,409, 1984.
60 **US Patent** 4,482,408, 1984.
61 **US Patent** 4,482,407, 1984.
62 **US Patent** 4,482,406, 1984.

63 **US Patent** 4,457,791, 1984.
64 **US Patent** 4,453,021, 1984.
65 **US Patent** 4,432,817, 1984.
66 **US Patent** 4,023,994, 1977.
67 **US Patent** 3,933,542, 1976.
68 Moore S K, *Chem. Week*, **161**, No.45, 1st Dec.1999, p.17.
69 Gan L H; Ooi K S; Goh S H; Gan L M; Leong Y C, *Eur. Polym. J.*, **31**, No.8, Aug.1995, p.719-24.
70 Vijayendran B R; Benecke H; Elhard J D; McGinniss V D; Ferris K F, Antec, Dallas, Texas, 6th-10th May, 2001, paper 604.
71 **US Patent** 3,970,628, 1976.
72 Tillekeratne M; Easteal A J, *Polym. Intl.*, **49**, No.1, Jan.2000, p.127-34.
73 Uniplex 542, Application in Polyvinylchloride, Unitex Chemical.
74 **US Patent** 6,512,036, 2003.
75 **US Patent** 5,430,108, 1995.
76 **US Patent** 5,300,812, 1994.
77 **US Patent** 4,605,694, 1986.
78 **US Patent** 4,085,080, 1978.
79 **US Patent** 5,958,993, 1999.
80 **US Patent** 5,206,404, 1993.
81 **US Patent** 4,714,771, 1987.
82 **US Patent** 4,559,184, 1985.
83 **US Patent** 4,482,506, 1984.
84 **US Patent** 4,363,882, 1982.
85 **US Patent** 4,207,225, 1980.
86 **US Patent** 4,139,487, 1979.
87 **US Patent** 4,111,882, 1978.
88 **US Patent** 3,945,891, 1976.
89 **US Patent** 3,936,410, 1976.
90 **US Patent** 3,931,367, 1976.
91 Tricresyl phosphate. International Program on Chemical Safety. Environmental Health Criteria 110.
92 Triphenyl phosphate. International Program on Chemical Safety. Environmental Health Criteria 111.
93 Mirci L E, *Mater. Plast.*, **33**, 2, p.105-111. 1996.
94 **US Patent** 5,686,055, 1997.
95 **US Patent** 5,661,204, 1997.
96 **US Patent** 5,463,147, 1995.
97 **US Patent** 5,462,986, 1995.
98 **US Patent** 5,468,419, 1995.
99 **US Patent** 5,369,162, 1994.
100 **US Patent** 5,189,105, 1993.
101 **US Patent** 4,871,715, 1989.
102 **US Patent** 4,695,649, 1987.
103 **US Patent** 4,316,832, 1982.
104 **US Patent** 4,291,127, 1981.
105 **US Patent** 4,229,586, 1980.
106 Wilson A S, **Plasticizers. Principles and Practice**. *The Institute of Materials*, London, 1995.
107 **US Patent** 5,965,648, 1999.
108 DBE Intermediates, E. I. du Pont de Nemours, 1995.
109 **US Patent** 6,111,004, 2000.
110 **US Patent** 4,504,652, 1985.
111 **US Patent** 4,322,505, 1982.
112 **US Patent** 4,166,056, 1979.
113 **US Patent** 4,108,820, 1978.
114 **US Patent** 4,069,517, 1978.
115 Gardner J H, Addcon 99, Paper 8 pp.1-4.
116 **US Patent** 5,688,850, 1997.
117 EPA PF-987. Notice of Filling a Pesticide Petition to Establish a Tolerance for a Certain Pesticide Chemical in or on Food.
118 Mirci L E, *Mater. Plast.*, **32**, 3-4, p. 169-174, 1995.
119 **US Patent** 4,123,411, 1978.
120 **US Patent** 5,217,649, 1993.

121 **US Patent** 4,996,284, 1991.
122 **US Patent** 6,249,928, 2001.
123 **US Patent** 4,218,357, 1980.
124 **US Patent** 6,194,498, 2001.
125 Sakai E, Yamada K, Ohta A, *J. Advanced Concrete Technol.*, **1**, p. 16-25, 2003.
126 Page M, Spiratos N, The role of superplasticizers in the development of environmentally-friendly concrete, Intern. Symp. Concrete Technol. Sustainable Develop., Vancouver, BC, Canada, April 19-20, 2000.
127 Tantawi S H, *Polym.-Plast. Technol. Eng*., **36**, 6, p. 863-872, 1997.
128 **US Patent** 6,441,054, 2002.
129 **US Patent** 4,137,088, 1979.
130 Adams R C; Petkus S L, Antec 2000.Conference proceedings, Orlando, Fl., 7th-11th May, 2000, paper 647.
131 Mirci L.E.; Terescu-Boran S; Istratuca G, *Mater. Plast.*, **35**, No.4, 1998, p.239-46.
132 Mirci L E; Boran S T; Istratuca G, *Mater. Plast*., **36**, No.1, 1999, p.13-20.
133 Mirci L E; Terescu S, *Mater. Plast*., **35**, No.1, 1998, p.29-36.
134 Mirci L E; Terescu S, *Mater. Plast*., **34**, No.2, 1997, p.97-104.
135 **US Patent** 4,327,021, 1982.
136 **US Patent** 5,489,646, 1996.
137 Lower E S, *Polym. Resin Technol*., **25**, 1, pp. 24-29, 1996.
138 Bos A; Punt I G M; Wessling M; Strathmann H, *J. Membrane Sci*., **155**, No.1, 1999, p.67-78.
139 Sanderson R D; Schneider D F; Schreuder I, *J. Appl. Polym. Sci.*, **57**, No.6, 8th Aug.1995, p.727-38.
140 Sanderson R D; Schneider D F; Schreuder I, *J. Appl. Polym. Sci.*, **55**, No.13, 28th March 1955, p.1837-46.
141 **US Patent** 5,356,986, 1994.
142 **US Patent** 6,348,563, 2002.
143 **US Patent** 4,051,095, 1977.
144 **US Patent** 4,123,413, 1978.
145 **US Patent** 4,143,092, 1979.
146 **US Patent** 6,118,012, 2000.
147 **US Patent** 6,403,702, 2002.
148 **US Patent** 6,437,032, 2002.
149 **US Patent** 5,952,411, 1999.
150 Mirci L E, *Mater. Plast*., **32**, No.1, 1995, p.20-5.
151 Mirci L E, *Mater. Plast*., **33**, No.1, March 1996, p.18-25.
152 **US Patent** 4,052,205, 1977.
153 **US Patent** 4,857,573, 1989.
154 **US Patent** 4,458,047, 1984.
155 **US Patent** 4,444,938, 1984.
156 **US Patent** 5,248,531, 1993.
157 Isley J M; Gott S L, *J. Vinyl Additive Technol*., **1**, No.4, Dec.1995, p.213-6.
158 **US Patent** 5,624,975, 1997.
159 Parmentier J, *Pitture Vernici*, **74**, No.18, Nov.1998, p.24/31.
160 **US Patent** 4,136,077, 1979.
161 **US Patent** 4,148,773, 1979.
162 **US Patent** 6,140,450, 2000.
163 **US Patent** 4,971,679, 1990.
164 **US Patent** 4,908,400, 1990.
165 **US Patent** 4,144,217, 1979.
166 **US Patent** 4,184,993, 1980.
167 **US Patent** 4,399,248, 1983.
168 **US Patent** 6,342,320, 2002.
169 **US Patent** 6,235,312, 2001.
170 **US Patent** 4,969,953, 1990.
171 **US Patent** 4,426,542, 1984.
172 **US Patent** 5,534,652, 1996.
173 **US Patent** 5,324,853, 1994.
174 **US Patent** 5,880,310, 1999.
175 Kuznetsova E V; Golland A E, *Intl. Polym. Sci. Technol.*, **24**, No.4, 1997, p.T/51-3.
176 Kuznetsova E V; Maksimenko E G; Kirilovich V I, *Intl. Polym. Sci. Technol*., **24**, No.2, 1997, p.T/54-5.
177 **US Patent** 5,532,405, 1996.
178 **US Patent** 5,688,848, 1997.
179 Horng-Jer Tai, *Polym. Eng. Sci.*, **39**, No.7, July 1999, p.1320-7.

180 **US Patent** 4,108,926, 1978.
181 **US Patent** 4,242,468, 1980.
182 **US Patent** 4,302,570, 1981.
183 **US Patent** 4,245,030, 1981.
184 **US Patent** 6,001,913, 1999.
185 **US Patent** 5,969,034, 1999.
186 White L A; Jonson S; Hoyle C E; Mathias L J, *Polymer*, **40**, No.23, 1999, p.6597-605.
187 Sasthav J R; Harris F W, *Polymer*, **36**, No.26, 1995, p.4911-7.
188 Pena J R; Hidalgo M; Mijangos C, *J. Appl. Polym. Sci.*, **75**, No.10, 7th March 2000, p.1303-12.
189 **US Patent** 5,939,160, 1999.
190 **US Patent** 5,464,903, 1995.
191 Ulyatt J, *Pitture Vernici*, **71**, No.11, June 1995, p.29-33.