

PLASTICIZERS IN VARIOUS INDUSTRIAL PRODUCTS

Typical components of each subchapter devoted to a particular group of products include:

- plasticizer types
- plasticizer concentrations
- reasons for addition (or expectations from plasticizers)
- technical advantages and disadvantages of plasticizers use
- effect of plasticizers on product properties and durability
- examples of formulations.

The information in these sections is based on the available open and patent literature with special attention given to the most recent applications as to form background characterizing modern use of plasticizers in industrial products.

13.1 ADHESIVES AND SEALANTS

13.1.1 PLASTICIZER TYPES

Adhesives

- dialkyl phthalate in two-component polyurethane adhesive^{91,102}
- diethyl phthalate in orthodontic adhesive⁶³
- dibutyl phthalate in laminating, elastomeric gel adhesive for capacitor rolls²³
- di-(2-ethylhexyl) adipate in adhesive for lamination of metal foil with resin film¹⁵ and in polyurethane potting material¹⁰⁶
- dioctyl phthalate in one-part curable polyurethane adhesive⁶¹
- diisononyl phthalate in automotive plastisol based on styrene copolymers¹⁰³
- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352) in delayed-tack adhesive⁶⁵
- dipropylene glycol dibenzoate in water-based wallboard adhesive,³⁶ in adhesive and coating for repairing plastic sheets,³⁸ in water-based adhesive,⁶⁴ and in polyvinylalcohol adhesives¹⁰⁸
- dipropylene/diethylene (50/50) glycol dibenzoate (Benzoflex 50) in water and heat resistant formulation,⁴³ in laminating adhesive,⁵⁷ and in water-based book-binding adhesive¹¹⁰
- acetyl triethyl citrate in hydrophilic adhesive for medications⁷⁶ and in biodegradable composition for papermaking and nonwoven production⁷⁷
- triethyl citrate in hydrophilic adhesive for medications⁷⁶
- epoxidized soybean oil in adhesive for lamination of metal foil with resin film¹⁵

- glycerin in paper adhesive based on polyvinylalcohol,¹⁴ in oral antifungal preventive,⁷⁸ in remoistenable maltodextrin adhesives,⁸⁹ and in casein film¹⁰⁰
- isopropyl myristate in hormone-delivering therapeutic system⁴⁶
- fatty acid ester of glycerin as a solid plasticizer of medical adhesives⁴⁸
- ester of higher fatty acid (C_{12} to C_{16}) with lower monovalent alcohol (C_1 to C_4) as a liquid plasticizer of medical adhesive⁴⁸
- polyoxyethylene-nonylphenol in hormone-delivering therapeutic system⁴⁶
- N-butyl benzene sulfonamide in polyamide composition¹⁰¹
- o,p-toluene sulfonamide in polyamide composition¹⁰¹
- hydrogenated mineral oil in structural adhesive⁶⁶
- mineral oil which is a mixture of naphthenic, aromatic, and paraffinic compounds (Catenex) used in adhesive mass for treating skin blisters, lesions and exudative wounds and burns⁷¹
- polyethylene glycol in cosmetic adhesive,³² in composition for sealing animal skin,⁶⁹ and in dental composition⁹²
- polyethylene glycol monooleate or monolaureate (Pycol 94) in water sensitive hotmelt adhesive⁴⁰
- polypropylene glycol in cigarette filters⁸⁶
- polypropylene glycol alkyl phenyl ethers (Plastilit 3060) in water resistant adhesive⁸²
- polyisobutylene in hydrocolloid medical adhesive²⁹
- polyester produced from hexanedioic acid and 1,4-butane diol and 1,2-propane diol (Uniflex 300) in anaerobic composition²⁴

Pressure-sensitive adhesives

- diethyl adipate in PSA used at low temperatures⁷⁰
- methoxy poly(ethylene glycol)⁴⁷ is added to wet-stick adhesive to improve its pressure-sensitive characteristics¹⁶
- glycerin in conductive adhesive for biomedical electrodes⁴⁷
- paraffinic mineral oil (white mineral oil) in roofing tape³⁹ and in transdermal therapeutic system (in combination with polyisobutylene)⁹⁸
- naphthenic process oil¹⁸
- mineral oil in transdermal patch⁸⁴
- polyisobutylene in roofing tape,^{28,37,39} in non-fogging film,²⁹ in transdermal drug delivery system,³¹ and in combination with paraffinic oil⁹⁸
- isopropyl myristate in transdermal patch⁵¹
- polyethylene glycol monooleate or monolaureate (Pycol 94) in PSA for low energy surfaces,⁴⁵ PSA used at low temperature conditions,⁷⁰ and in static charge reducing film¹⁰⁹
- ethylamine toluenesulfone in alkali-soluble adhesive⁴¹
- polyester azelate in PSA containing automotive laminate⁷²
- hydrophilic and hydrophobic plasticizer in acrylic-containing pressure sensitive adhesive¹²⁹ which acts very well on both hydrophilic and hydrophobic surfaces

Hotmelts

- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352)^{4,44} is a solid plasticizer frequently used in hotmelts based on ethylene vinyl acetate copolymer, EVA,⁴ in bookbinding adhesives,⁷⁴ in packaging adhesives,⁸⁷ in high resistant adhesives,⁹⁷ and in carton seals¹⁰⁵
- dipropylene glycol dibenzoate in hydrophilic hot melt adhesives²⁷ and in compostable products containing biodegradable adhesives⁹⁶
- di-(2-ethylhexyl) phthalate in heat sealable tapes,⁵⁰ in traffic marking compositions,⁸¹ and in adhesives having long open time (2 h)⁹³
- trimellitic plasticizer in pressure sensitive adhesive tape¹³⁰
- dipropylene glycol dibenzoate in alkali soluble compositions⁶⁷
- polyisobutylene in hotmelts for nonwoven applications,⁴⁹ in formulations for nonwoven, disposable articles,⁷⁵ and in disposable soft articles⁹⁵
- mineral oil having low aromatic content in SBS copolymer^{11,27} and in formulations for nonwoven, disposable articles⁷⁵
- paraffinic oil in adhesives for disposable medical goods,⁵⁶ in cohesively failing adhesives,⁵⁸ and in packaging adhesives⁸⁷
- polyethylene glycol mono- and di-laureates in water sensitive formulations⁷³
- a combination of anionic (sodium dioctyl sulfosuccinate), cationic (fatty amine quaternary ammonium salt), and polar nonionic (either benzyl butyl phthalate or glycol dibenzoate) is used for water sensitive hotmelt adhesives (adhesive applied as hotmelt but moisture activated; e.g., envelope sealing adhesive)²²

Sealants

- benzyl butyl phthalate in roof sealant compositions¹³
- dioctyl phthalate in polysulfide-based polyurethane sealants for insulating glass^{26,34}
- di-(2-ethylhexyl) phthalate in automotive weatherstrip sealants⁵⁵
- diisodecyl phthalate in self-levelling plastisol composition for automotive applications¹⁷
- chloroparaffin having long chain with 52 and 70 wt% Cl in primary sealants for insulating glass units¹² and in polysulfide-based polyurethane sealants for insulating glass^{26,34}
- polyisobutylene in silicone²⁰
- polyorganosiloxanes (non-reactive) in waterborne silicone sealants,³⁵ in silicone edge sealants,⁷⁹ and in sealants which have increased tooling time⁸³
- epoxidized soybean oil in oxygen scavenging sealant composition (sealant contains particles of oxygen scavengers dispersed in plasticizer; it provides hermetic seal)⁴²
- hydrophilic plasticizer in self-levelling silyl-terminated sealant¹²⁷
- C4 to C8 alkyl terephthalate¹²⁸

Large number of different resins and thus large number of plasticizers are used in adhesives and sealants. First general observation is that phthalates are used much less frequently in recent inventions than in products existing in the market. This is due to sensitivity to these plasticizers in the market place. The second general observation is that there is a little difference in plasticizer choice for different groups of adhesives. Perhaps the only

more specific is use of solid plasticizers and in many cases their combinations with liquid plasticizers in hotmelts. Also, in pressure sensitive adhesives more attention is given to the compatibility of plasticizer with tackifying resin than with binder. It can also be observed that benzoates, mineral oils of various compositions, and polyisobutylenes (or polybutenes as they are also called) are groups of plasticizers which currently experience growth.

13.1.2 PLASTICIZER CONCENTRATION

- benzyl butyl phthalate: up to 5 wt%¹³
- diallyl phthalate: 22 to 25 wt% in two-component polyurethane adhesive⁹¹
- dibutyl phthalate: 67.3 wt% in adhesive to laminate foil and film layers in capacitor roll²³
- di-(2-ethylhexyl) phthalate: 6 to 8 wt% in adhesive of heat sealable tape,⁵⁰ 20 wt% in automotive weatherstrip sealant,⁵⁵ 1 to 5 wt% in traffic marking composition,⁸¹ up to 30 wt% in hotmelt having long open time,⁹³ and 30 wt% in polyurethane potting material¹⁰⁶
- dioctyl phthalate: 25 to 32 wt% in one-part curable polyurethane adhesive⁶¹
- diisooctyl phthalate: 15 to 25 wt% in insulating glass adhesive³⁴
- diisononyl phthalate: 100 phr (or 33 wt%) in plastisol for automotive applications¹⁰³
- diisodecyl phthalate: 110 phr in PVC plastisol for automotive self-levelling sealants application¹⁷
- di-(2-ethylhexyl) adipate: up to 5 wt% in laminating adhesive for metal foil and resin film¹⁵
- 1,4-cyclohexane dimethanol dibenzoate: 5 to 20 wt% in heat resistant hotmelt⁹⁷ and 40 wt% in carton hotmelt seal¹⁰⁵
- dipropylene glycol dibenzoate: 5 to 7.5 wt% in hydrophilic hotmelt adhesive,²⁷ 10.5 wt% in water-based wallboard adhesive,³⁶ 2 to 5 wt% in adhesive for plastic sheet repair,³⁸ 18 wt% in alkali-soluble hotmelt,⁶⁷ 20 to 25 wt% in compostable adhesive,⁹⁶ and 8.5 wt% in polyvinylalcohol adhesive¹⁰⁸
- dipropylene/diethylene (50/50) glycol dibenzoate (Benzoflex 50): 15 wt% in water and heat resistant adhesive⁴³ and 5 to 8 wt% in bookbinding adhesive¹¹⁰
- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352): 20 wt%⁴⁴ and up to 25 wt% in composition with liquid plasticizer in packaging hotmelts⁸⁷
- acetyl triethyl citrate: 27 phr in biodegradable resin composition⁷⁷
- citrate plasticizer: 1-50 phr in adhesive sheet having acrylic ester copolymer¹³¹
- epoxidized soybean oil: up to 1 wt% in laminating adhesive for metal foil and resin film¹⁵
- glycerin: 1 wt% in oral antifungal preventive,⁷⁸ 8 wt% in maltodextrin adhesive,⁸⁹ and 5 to 15 wt% in casein film¹⁰⁰
- polyisobutylene: 14 to 25 wt% in silicone sealant,²⁰ 5 to 9 wt% in roofing tape,^{28,37} 2 to 25 wt% in medical hydrocolloid adhesive,²⁹ 35 to 65 wt% in transdermal drug delivery system,³⁰ 10 to 25 wt% in hotmelt adhesive for polyolefins,³³ up to 30 wt% in hotmelt for nonwovens,^{49,76} 20 to 25 wt% in disposable soft articles,⁹⁵ and 10 wt% in transdermal therapeutic system (in addition to 20 wt% of paraffinic oil)⁹⁸

- mineral oil (low aromatic content): 5-35 phr (amount of plasticizer depends on type and amount of tackifying resin) in hot melts from SBS copolymer,¹¹ 5 to 15 wt% in formulation for nonwoven, disposable articles,⁷⁵ 10 to 40 wt% in transdermal patch⁸⁴
- mineral oil (naphthenic): 8 to 16 wt% of pressure sensitive adhesive¹⁸ and 15 to 20 wt% in hydrophilic hot melt adhesive²⁷
- paraffinic oil: 10 to 30 wt% in adhesive for disposable medical goods,⁵⁶ 30 to 50 wt% in cohesive failing adhesive,⁵⁸ 5 to 15 wt% in packaging hotmelt (in addition to solid plasticizer),⁸⁷ 20 wt% in transdermal therapeutic system (in addition to 10 wt% of polyisobutylene)⁹⁸
- mineral oil (a mixture of naphthenic, aromatic, and paraffinic compounds) (Catenex): 2 to 25 wt%⁷¹
- polyethylene glycol: up to 5 wt% in adhesive film used to reduce electric charges¹⁰⁹
- polyethylene glycol monooleate or monolaureate (Pycol 94): 3 to 10 wt% in pressure sensitive adhesive for low energy surfaces⁴⁵
- polypropylene glycol alkyl phenyl ethers (Plastilit 3060): 20 phr in water resistant adhesive⁸²
- chloroparaffin: 15 to 25 wt% in insulating glass adhesive³⁴
- polyethylene glycol: above 40 wt% adhesive has pressure-sensitive properties³²
- polymeric (polyester): from 1 to 6 wt% in anaerobic adhesive²⁴
- polyester azelate having molecular weight greater than 7,000 daltons: 26 to 36 wt% in PSA adhesive for automotive laminate⁷²
- polyorganosiloxanes (non-reactive): up to 15 wt% in silicone sealants³⁵ 10 wt% in sealant having longer tooling time⁸³

Use of plasticizers is very popular in adhesives and sealants but they are used in moderation. Some plastisols, self-levelling compositions, and cohesively failing products are typical exceptions. They require high concentration of plasticizers for their intended performance.

13.1.3 REASONS FOR PLASTICIZER USE

- viscosity control^{33,49,69,75}
- modification of rheological properties⁵³
- viscosity reduction of polyurethane polymer during its synthesis or dispersion in final formulation⁶¹
- substantial increase in viscosity of water-based emulsions^{57,64}
- decreasing the glass transition temperature of polymer^{14,18}
- making material more flexible^{69,72,74}
- increasing elongation
- lowering softening point to improve coating smoothness⁴¹
- to lower application temperature of adhesive
- regulation of skin time of sealant²⁰
- regulation of sensitivity to water by addition of either hydrophilic or hydrophobic⁴³ plasticizers
- water soluble plasticizers (e.g., polyethylene glycol monooleate or monolaureate) induce water sensitivity⁴⁰

- improved adhesion to unreactive and slow-to-cure metal substrates (polyester plasticizer)²⁴
- increased adhesion to polyolefins (e.g., 1,4-cyclohexane dimethanol dibenzoate)⁷⁴
- to obtain non-fogging materials (selected plasticizers)^{54,72}
- imparts softness, thereby decreases skin irritation in medical adhesives⁴⁸
- increased effectiveness of the anti-hypersensitivity agent in dental composition⁹²
- promoting ductile failure⁶³
- regulation of tackiness³²
- improvement of adhesion of paint⁹⁰
- to increase vibration damping properties⁵³
- acts as a carrier for drug component⁸⁴
- acts as liquid binder of cigarette filter⁸⁵
- high dielectric constant²³
- high breakdown strength²³
- approval for use in food, drugs, or medical devices
- solvent replacement⁹⁴

Plasticizers use in adhesives and sealants is much less related to the typical expectations from plasticizers such as lowering glass transition temperature and making material more flexible. In this group, desired performance characteristics of plasticizers are dominated by their low volatility and low viscosity. It is also frequent in this group that such disadvantage of plasticizer incorporation as its migration is a virtue here and special attention is given to the selection of plasticizer and so-called tackifying resin that together they form a tacky surface rather undesired in most other groups of products. Plasticizers also perform here many secondary function very important for the qualities required from these products, such as promotion of migration of some active substances (especially in medical applications), lowering reaction rate, sensitivity to water, etc.

13.1.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- decrease glass transition temperature of polymer¹⁴
- easy adjustment of mechanical properties such as elongation, modulus, adhesion, failure type (cohesive vs. adhesive), impact strength, etc.⁹
- small addition of plasticizer (up to 1 wt%) increases open time of polychloroprene adhesive¹⁰
- increase in migration rate of indicator dye to the surface in paper time indicator¹⁴
- improved adhesion of silicone sealant and oil resistance by replacement of low molecular silicone oil by polyisobutylene²⁰
- viscosity control²⁷
- viscosity of water-based emulsion can be increased 3 to 10 times by addition of benzoate plasticizer^{57,64}
- some plasticizers such as diethyl adipate and polyethylene glycol monooleate or monolaureate (Pycol 94) are transparent to UV radiation. These plasticizers do not interfere with curing of acrylate copolymers by radiation⁷⁰

Disadvantages

- low molecular weight plasticizers may slowly volatilize contributing to indoor pollution (so-called “sick house syndrome”)⁸
- low molecular weight plasticizer outgasses which changes mechanical properties of products and contributes to fogging³⁰ (use of high molecular weight plasticizers, e.g., polymeric plasticizers or polyisobutylenes) eliminates this problem
- in polyurethane sealant applications low molecular weight plasticizers migrate to surface, increase surface tack and contribute to the dirt pickup⁹
- migration of low molecular weight plasticizers to sealant surface affects properties of paints and its overall paintability⁹
- extensive migration or bleeding of plasticizer result in loss of wet-stick properties of adhesive (in order to avoid it, plasticizers compatible with polymer are used)¹⁶
- phthalate plasticizers used together with stannous catalyst and silyl-group containing compounds reduce shelf-life of one-component products²¹
- lowering service temperature of hotmelt adhesive^{27,49}
- decreasing adhesive strength of hotmelt adhesive²⁷

Advantages and disadvantages of use of certain plasticizer are case sensitive and should be used in context of selected plasticizer and needs of final product.

13.1.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352) melts at 118°C.⁴ Because it increases wetting properties of melted glue it increases adhesion to various substrates. EVA hotmelts containing this plasticizer have excellent adhesion to glass, wood, and paper.⁴ The adhesion of hotmelt to substrate depends on crystallization of 1,4-cyclohexane dimethanol dibenzoate. At low crystallization, adhesion is very good and at high crystallization the adhesion is rapidly decreased. This solid plasticizer is also used in delayed-tack adhesives. At normal temperatures, adhesive does not have tack but once activated by increased temperature it remains very tacky for a long time.⁶⁵ This type of adhesives are called “heat-sensitive adhesives”.

Pressure sensitive adhesives include in formulation tackifying resins which are required for their performance. Frequently tackifying resins increase glass transition temperature of matrix polymer and means are needed to lower glass transition temperature of product. Plasticizers are used in these formulations to perform dual purpose: compensation or lowering glass transition temperature and making tackifying resin more effective. It is very essential in these formulations to select type and amount of plasticizer which is compatible with tackifying resin.⁴⁵

Water sensitivity and solubility can be conveniently regulated by the use of a combination of plasticizers. In hotmelt which is water sensitive two groups of plasticizers are used in different proportions depending on required properties.⁷³ Larger amounts of water soluble plasticizers such as polyethylene glycol mono- and di-laureates increase water sensitivity. Addition of larger amounts of water insoluble plasticizers, such as 2-ethylhexyl diphenyl phosphate or butyl benzyl phthalate increases hydrophobic properties of hotmelt.⁷³

Addition of plasticizer to polyurethanes can be done in several ways: in the beginning of synthesis of prepolymer, at the last stages of synthesis, and during adhesive/sealant compounding. Each method has some advantages. Addition of plasticizer in the beginning

of prepolymer synthesis allows for better cooling (lower viscosity) and thus speeds up process of isocyanate addition and thus polycondensation. Plasticizer can also be added when exotherm recedes and temperature drops, this will stop reaction and reduce cooling time of prepolymer before transfer.¹⁰² Addition during compounding stage reduces reactor volume required for smooth operation. In two component system plasticizer can be added to either part. Usually two considerations are important: increasing volume of curative or maintaining similar viscosities of both parts for more effective mixing. In either case plasticizer added must be moisture free.¹⁰⁴

In some products for medical, dental, drug, and food contact applications, the so-called "toxicologically acceptable plasticizers" must be used. This means that plasticizers are suitable in their toxicity profile for administration to humans and/or lower animals. Plasticizers that may be used in these compositions include dimethyl phthalate, diethyl phthalate, dioctyl phthalate, glycerin, diethylene glycol, triethylene glycol, Igepal, Gafac, sorbitol, tricresyl phosphate, dimethyl sebacate, ethyl glycolate, ethyl phthalyl ethyl glycolate, o- and p-toluene ethyl sulfonamide, glycerin, and their mixtures.⁶⁸

In the production of a tobacco filter, a plasticizer (e.g., triacetin, triethylene glycol diacetate, triethylene glycol dipropionate, dibutyl phthalate, dimethoxyethyl phthalate, triethyl citrate, etc.) is commonly added for shape retention of the filter plug and for insuring the firmness or hardness necessary for cutting out filter tips from the plug. The filaments are partly fused together by the plasticizer. Thus, the plasticizer plays the role of a binder interbonding the cellulose ester filaments at random locations. As a consequence, if the cigarette butt is discarded, it takes a long time for the filter plug to disintegrate itself, doing aesthetic harm to the environment and adding to the pollution problem.⁸⁵ Recent invention proposes to replace plasticizer by water soluble polymer (polyvinylalcohol). This replacement improves dramatically disintegration time of tobacco filter.⁸⁵ Another invention solves problem with the use of plasticizer.⁸⁶ Long disintegration time is attributed to hydrophobic properties of the listed above plasticizers and their potential solvent effect on cellulose acetate, a fiber used in filter production. When any of currently used plasticizer is replaced by a blend containing 90 wt% polypropylene glycol having molecular weight of 3400 daltons and 10 wt% triacetin, the disintegration time rapidly decreases because polypropylene glycol is water soluble and it is immediately removed from filter when discarded.⁸⁶

13.1.6 EXAMPLES OF FORMULATIONS

Water-based, wallboard adhesive:³⁶

Polyvinyl acetate emulsion	43.67 wt%
Thickener (modified cellulose)	0.30
Defoamer	0.03
Plasticizer (dipropylene glycol dibenzoate) ⁴	10.50
Surfactant (alkylphenol-ethylene oxide)	0.35
Dispersant (aromatic sulfonic acid, sodium salt)	0.07
Dispersant (inorganic polyphosphate)	0.35
Stabilizer (ethylene glycol)	0.70
Organic preservative	0.03
Calcium carbonate (fine)	23.00
Calcium carbonate (coarse)	20.00

Mineral spirits	1.00
Adhesive for plastic sheet repair: ³⁸	
Ethyl acetate	36.39 wt%
Cyclohexanone	36.39
Acrylonitrile-butadiene copolymer (Nipol 1022)	11.48
Terpene phenol resin (Nirez V2040)	11.48
Dibenzoate plasticizer (Benzoflex S312)	3.63
Antioxidant (butyl zimate)	0.32
Optical brightener (Uvitex OB)	0.31
Roofing tape: ³⁹	
EPDM (Trilene 77)	70 parts
Styrene-ethylene/propylene (Kraton G-1701)	50
Polyisobutylene (Vistanex CP-24)	80
Polyethylene wax	30
Antioxidant	2
Carbon black	20
Treated calcium carbonate	750
Silica	20
Tackifier(s)	95
Lime	20
Oleic acid	2
Organoclay	40
Mineral oil	40
Naphtha	100
VM&P naphtha	200
Hydrophilic hotmelt adhesive: ²⁷	
Tall-oil rosin ester (Unitac R100L)	57.5 wt%
SBS copolymer (Stereon 840A)	20
Mineral oil (Kaydol)	10
Dipropylene glycol dibenzoate (Benzoflex 9-88)	7.5
Nonionic surfactant (Atmer 688)	4
Antioxidant (Irganox 1010)	1
Hotmelt adhesive with solid plasticizer: ⁴⁴	
SIS block copolymer (Europrene Sol T 190)	19.4 wt%
Antioxidant (Irganox 1076)	0.49
Aliphatic tackifying resin (Regalrez 1094)	29.1
Styrenated terpene tackifying resin (Zonatac 105LT)	29.1
Cyclohexane dimethanol dibenzoate (Benzoflex 352)	18.9
Hotmelt for nonwovens: ⁴⁹	
Resin (Eastotac H-130R)	29.9 wt%
Polybutylene (polyisobutylene, 800 daltons)	19.9

Amorphous polyolefin (Rextac 2115)	39.8
Wax (Epolene N15)	9.5
Antioxidant (Irganox 10100)	0.9

Hotmelt for sealing cartons:¹⁰⁵

Tackifying resin (Escorez 7312)	48.0 parts
Antioxidant (Irganox 1076)	1.0
Ethylene vinyl acetate (Elvax 150)	10.0
Plasticizer (Benzoflex 352)	39.9

Pressure sensitive hotmelt:⁵⁸

SEBS copolymer (Kraton G1726)	20.0 wt%
Tackifier (Kristalex 3070)	40.0
Paraffin oil (Kaydol)	39.5
Antioxidant (Irganox 1010)	0.5

Silicone sealant (oil resistant):²⁰

Silanol fluid	52.44 wt%
Fumed silica (Aerosil R974)	8
CaCO ₃ (Socal 322)	10
TiO ₂	1
Polyisobutylene (Indopol L-14)	24
Vinyl trioximino-silane	4
Aminosilane	0.5
Catalyst (UL-28)	0.1

Silicone sealant with longer tooling time:⁸³

Base polymer	53.00 wt%	61.00
Stearic acid treated CaCO ₃	20.00	10.00
SiO ₂	10.00	12.00
Ethyltriacetoxysilane (crosslinker)	4.80	4.80
Catalyst	0.0257	0.0257
Polydimethylsiloxane (plasticizer)	10.00	10.00
Adhesion promoter	1.17	1.17
Carbon black (pigment)	1.00	1.00
<i>Tooling time, sec</i>	350	90

13.2 AEROSPACE

Materials used in external parts of aircraft are exposed to very demanding conditions such as very low pressure, large temperature variation within a short period of time, large stresses, UV, aggressive chemical liquids.¹²⁶ Materials used in spacecraft are exposed to still higher temperature changes, intensity of UV radiation, presence of highly degrading radiation wavelengths, proton, cosmic, and electron radiations, atomic oxygen and vacuum.¹²⁶ It is quite obvious that materials which are considered to have low volatility on Earth level are quite volatile even at altitudes of commercial aircraft cruising. All these

extraordinary conditions require special materials. Because construction and repairs are performed on sea level all restrictions regarding health and safety and environmental impact also apply to these materials which further complicates material design. There is little information available on aerospace materials because it is rarely published or patented. Information on a few known innovations is reported below.

Average large aircraft needs more than a million fasteners made from a ferrous alloy. These were installed using wet sealant. Curable organic coating is proposed which is based on plasticized phenolic resin.¹¹⁴

Partially hydrogenated terphenyl plasticizer (HB-40) is used in aerospace sealant based on polyurethane.¹¹⁵ Sealants used by aerospace industry require fuel resistance, long potlife, and high temperature resistance.¹¹⁸ Some applications of these sealants include lining of fuel tank, electrical potting and encapsulant compounds. Polymers made from reaction of a polythiol and polyvinyl ether monomer are plasticized by phthalate esters, chlorinated paraffins, and hydrogenated terphenyls.¹¹⁸ Sealants and linings of fuel tanks contain 6 wt% of hydrogenated terphenyl.¹²⁰ The purpose of plasticizer addition is to decrease glass transition temperature.

Corrosion inhibiting polysulfide sealants are considered the most cost effective means of sealing aircraft. These sealants use hydrogenated perphenyl plasticizer (HB-40).¹²¹ It is expected that sealants have excellent fuel resistance, low-temperature flexibility, adhesion to variety of surfaces, UV, moisture and electrical resistance, and good vibration-damping properties.¹²¹ Five to twenty weight percent of phthalate plasticizer is used in flexible epoxy encapsulating material.¹¹⁹ Chlorinated paraffin with either 52 or 70% chlorine in long chain paraffin was used in one-component insulating glass sealant.¹²⁴

Solid propellants are used extensively in aerospace industry to power missiles and rockets for military, commercial, and space applications. Propellant may comprise from 1 to 3 wt% of plasticizer such as dioctyl adipate.¹¹⁶

Several industries including aerospace use rapid prototyping. Prototypic materials use polyethylene glycol having molecular weight of 600 daltons as plasticizer for poly(2-ethyl-2-oxaline), PEO, a polymer used for making prototypes. Plasticizer enhances overall water solubility of PEO and its dissolution rate.¹¹⁷

Microbiological corrosion is also affecting space materials which contain additives, including plasticizers.¹³² Effect of phthalate plasticizers was discussed.¹³²

Alkyl benzyl phthalate is used in windshield adhesive used in aircrafts.^{133,135} The so-called hump seal invented in this application is two-component product containing also other additives.^{133,135}

Several plasticizers can be used in sealant, such as benzyl butyl phthalate, chlorinated paraffin, hydrogenated terphenyl, or hydrocarbon.¹³⁴ This sealant is suitable for double glazing, aircraft, and civil engineering.¹³⁴

13.3 AGRICULTURE

Seeds are coated by polydextrose-based coating containing polyethylene glycol having molecular weight of 8,000 daltons (5 wt%) and triacetin (5 wt%).¹³⁶ Slow release granules containing pesticides are prepared by blending with DOP plasticized PVC and melt extrusion.¹³⁷ Water dispersible granules are based on polyvinylpyrrolidone plasticized with 2 wt% of glycerin.¹³⁷

Glycerin triacetate, tributyl acetyl citrate, and diglycerin tetraacetate were used as plasticizer of biodegradable resin compound based on biodegradable polyester.¹³⁸ Polyester polymer used in invention is based on poly(lactic acid).¹³⁸

13.4 AUTOMOTIVE APPLICATIONS

13.4.1 PLASTICIZER TYPES

- ethylene vinyl acetate copolymers for low fogging interior products¹³⁹
- a combination of diphenyl isodecyl phosphate and tributyl citrate in chlorine-free plastisols¹⁴⁵
- diphenyl 2-ethylhexyl phosphate in automotive sealant¹⁶²
- dioctyl phthalate in laminated glass containing ultrafine particles providing UV absorption and heat insulation¹⁴⁸
- diisodecyl phthalate in self-levelling plastisol used for corrosion protection^{146,153}
- C₉ to C₁₁ phthalate in compound for primary, insulating cable¹⁵⁰
- diisodecyl adipate in seals and gaskets¹⁴⁷
- dipropylene glycol dibenzoate in automotive sealant¹⁶²
- triethylene glycol di-(2-ethylhexyl) butyrate in laminated glass containing ultrafine particles providing UV absorption and heat insulation¹⁴⁸
- benzoate plasticizer in material having improved acoustic properties¹⁶⁹
- mineral oil in seals and gaskets¹⁴⁷
- mineral, naphthenic oil to seal and coat steel substrates¹⁶⁰
- 1,2-propylene glycol adipate having molecular weight greater than 7,000 daltons (G-59) in pressure sensitive adhesive of exterior laminate¹⁵⁶
- trimethylol trinitrate as energetic plasticizer in propellant for air bag system¹⁵⁷
- 9-methylenenodecane and 2-decyl-2-oxyloxirane¹⁶⁵
- Leona made by Asahi Kasei in polyamide-6 tubing^{166,167}
- trimellitate+sebacate in PVC composition resistant to fogging¹⁷⁰
- trimellitate plasticizer in air bag doors¹⁷¹

13.4.2 PLASTICIZER CONCENTRATION

- a combination of diphenyl isodecyl phosphate and tributyl citrate: 80 phr of methyl and butyl methacrylate copolymer¹⁴⁵
- diphenyl 2-ethylhexyl phosphate: 28 wt% in automotive sealant¹⁶²
- dioctyl phthalate: 30 wt% in laminated glass^{148,149,168}
- diisodecyl phthalate: 25 to 35 wt% in self-levelling plastisol¹⁵³
- dipropylene glycol dibenzoate: 28 wt% in automotive sealant¹⁶²
- triethylene glycol di-(2-ethylhexyl) butyrate: 30 wt% in laminated glass^{148,149}
- 1,2-propylene glycol adipate: 4 wt% in pressure sensitive adhesive¹⁵⁶
- trimethylol trinitrate: 10-15 wt% in propellant for air bag system¹⁵⁷
- naphthenic oil: 140 phr in steel coating material¹⁶⁰
- non-functionalized plasticizer: up to 20 wt% in PE and PP parts¹⁶⁴

13.4.3 REASONS FOR PLASTICIZER USE

- lowering gelation and fusion temperatures¹⁵³
- improving flow properties¹⁵³
- enhancing elongation¹⁵⁶

- improvement in sound deadening of automotive carpets¹⁴⁴
- sound absorbing glazing for automotive windshield¹⁵²
- improvement of compression set of material for seals and gaskets in windows, doors, hoods and trunks¹⁴⁷
- dispersion of ultrafine filler^{148,149}
- maintaining breaking resistance of cable insulation at low temperatures¹⁵⁰
- thixotropic properties¹⁶⁵

13.4.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- low fogging (material passes 90% optical transmission test after at least 3 h at 120°C)^{139,143}
- non-bleeding plasticizers in brake tubing system prevent from reduction of tube cross-section which ultimately leads to reduced brake performance¹⁴⁰
- low freezing point¹⁵⁰

Disadvantages

- material for interior components contains volatile ingredients¹³⁹
- material for interior components contains ingredients which react with each other producing volatile components¹³⁹
- plasticizer-induced volatile haze in paint coat¹⁵⁶
- plasticizer migration¹⁵⁶
- interlayer adhesion failure¹⁵⁶

13.4.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Excellent TPEs have been obtained from polypropylene and EPDM plasticized with monomeric tallates and sebacates.¹⁴¹ Plasticizer affects only amorphous phase in polypropylene therefore upper service temperatures, characteristic of polypropylene, are maintained. Simultaneous plasticization of both component polymers (Figure 13.1) resulted in supertough material.¹⁴¹ TPEs were developed for rack and pinion boots, airbag door covers, and seals for low service temperature.

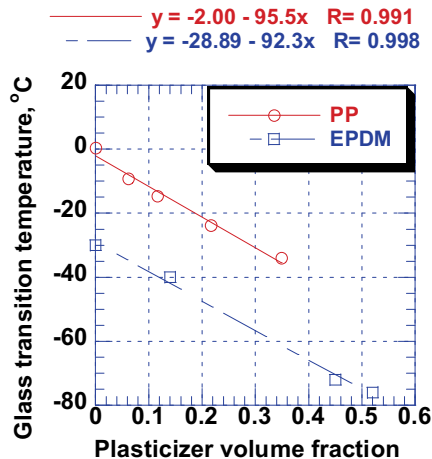


Figure 13.1. Effect of dioctyl sebacate volume fraction on glass transition temperature of EPDM and polypropylene. [Data from Ellul M D, *Rubber Chem. Technol.*, 71, No.2, May/June 1998, p.244-76.]

In recent years, the biggest changes were made to instrument panel and dashboard (also called recently by design engineers as the cockpit modules). These changes were first of all directed towards elimination of fogging and leaching out of volatiles subsequently deposited on the inside of windscreen, typical of previously used systems containing low molecular weight plasticizers. In addition, greater energy absorption, reduction in noise and vibration, and recyclability were the driv-

ing forces behind the changes.¹⁴³ Not only dashboard but other components of car interior were modified to reduce fogging and to increase recyclability.

Thermal desorption, GC/FID, and GC/MS coupled with solid phase micro-extraction were used to compare VOC in leather and artificial leather containing cars.¹⁶³ VOC varied from detection limit of a few $\mu\text{g}/\text{m}^2$ to thousands $\mu\text{g}/\text{m}^2$.¹⁶³ Type of trim affected reading but results depended on make.¹⁶³ Temperature increase in car interior increased VOC concentration.¹⁶³ Plasticizers were detected among additives forming VOC.¹⁶³ VOC concentration increased indoor guidelines but was decreasing with time of car use.¹⁶³

13.5 CEMENTITIOUS MATERIALS

13.5.1 PLASTICIZER TYPES

- sulfonated naphthalene formaldehyde^{187,189,190} (Conplast-430¹⁷³ Daracem 19¹⁸²) – a superplasticizer
- polyether grafted polyacrylate¹⁹⁰
- sodium salt of sulfonated phenylene formaldehyde¹⁷⁷
- sodium salt of polystyrene sulfonate condensate¹⁷⁷
- ligninosulfonate (Conplast-431) – retarder and plasticizer^{173,190}
- tannins and their products of sulfonation¹⁷⁵
- polycarboxylic acid based (Adva)¹⁸⁰
- melamine formaldehyde condensate (Melment F-10) – plasticizer/water reducer¹⁸³
- styrene-maleic anhydride copolymer (Rheobuild 3520) – superplasticizer^{185,188}
- casein¹⁹¹
- terpolymers¹⁹²

13.5.2 PLASTICIZER CONCENTRATION

- sulfonated naphthalene formaldehyde: 0.3 wt% of cement;¹⁷³ 0.25 wt% of sodium salt per dry cement;¹⁷⁷ and 0.4 wt% of dry cement in prefabricated buildings¹⁸²
- sulfonated phenylene formaldehyde, sodium salt: 0.25 wt% of dry cement¹⁷⁷
- ligninosulfonate (Conplast-431): 0.3 wt% of cement¹⁷³
- tannin: 0.25 wt% of dry cement¹⁷⁵
- polycarboxylic acid based (Adva): 0.06 to 0.1 wt% of cement¹⁸⁰
- styrene-maleic anhydride copolymer: 1 wt% of cement in spraying composition;¹⁸⁴ 0.8 wt% of cement¹⁸⁸

13.5.3 REASONS FOR PLASTICIZER USE

- reduction in water requirement^{173,175,178,180}
- improved hydration and its rate¹⁷⁵
- increased workability^{173,174,175}
- improved strength^{173,175}
- increased compressive strength^{173,174,177}
- improved durability¹⁷³
- improved surface texture¹⁷²
- total pore volume is decreased in the presence of superplasticizer¹⁷⁷
- restores flowability of mixture¹⁸⁷

13.5.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- improvement in fire-resistance of concrete¹⁷²
- decrease in viscosity of concrete mixture¹⁷⁵
- superplasticizers do not affect pore size¹⁷⁷
- superplasticizers do not affect phase composition¹⁷⁷

Disadvantages

- decreased degree of crystallinity of hydrates formed¹⁷²
- plasticizers (but not most superplasticizers) retard setting and early strength development of concrete¹⁷⁵
- ligninosulfonate-based and other superplasticizers delay setting time^{178,187}
- melamine-based superplasticizer exhibits bleeding¹⁷⁸
- plasticizers (but not superplasticizers) reduce final strength¹⁷⁵
- too large amount of superplasticizer (e.g., sulfonated naphthalene formaldehyde) may result in extensive shrinkage¹⁸⁵
- too large concentration of superplasticizer may prevent hydration and thus destroy binding ability of cement¹⁸⁹
- too low concentration of superplasticizer shortens setting time but increases viscosity¹⁸⁵

13.5.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Two main groups of products are discussed in this section: plasticizers and superplasticizers. Plasticizers are rheology modifying agents which increase plastic characteristics in cementitious mixtures.¹⁸⁹ Many types of the product are included here, such as cellulose derivatives (methylhydroxyethylcellulose, hydroxymethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose), starch based materials

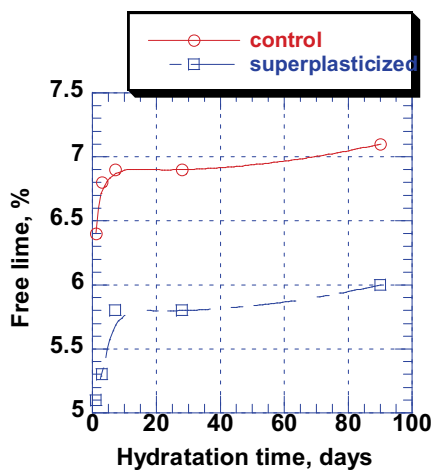


Figure 13.2. Free lime in concrete with and without 0.6 wt% of Complants-340 vs. hydration time. [Data from Tantawi S H, *Polym. Plast. Technol. Eng.*, **36**, No.6, 1997, p.863-72.]

(amylopectin, amylose, sea-gel, starch acetates, starch hydroxyethyl ethers, ionic starches, long-chain alkylstarches, dextrans, amine starches, phosphate starches, and dialdehyde starches), protein based materials, and synthetic products (polyvinyl pyrrolidone, polyethylene glycol, polyvinylalcohol, polyvinylmethyl ether, polyacrylic acid, polyacrylic acid salts, polyvinylacrylic acids, polyvinylacrylic acid salts, polyacrylimides, and ethylene oxide polymers).¹⁸⁹ It is quite evident from this list that many natural products were selected in order to obtain environmentally friendly mixtures.

Plasticizers thicken the cementitious material and add lubrication to make it flow. They are used in amounts from 0.1 to 2 wt% of cement. Plasticizers and, dis-

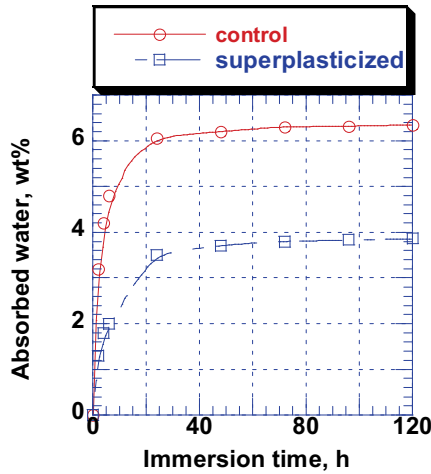


Figure 13.3. Absorbed water by concrete with and without sulfonated melamine and formaldehyde condensate superplasticizer vs. immersion time. [Data from Ray I; Gupta A P; Biswas M, *Cement Concrete Composites*, 17, No.1, 1995, p.9-21.]

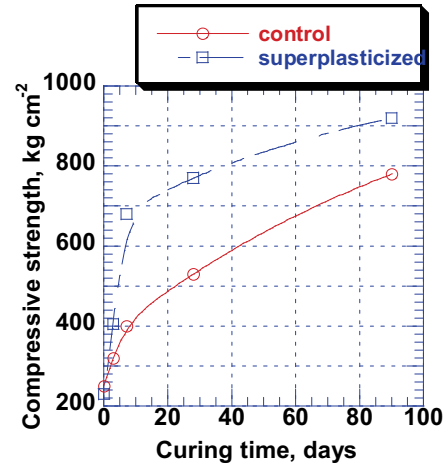


Figure 13.4. Compressive strength of concrete with and without superplasticizer (0.25 wt% of sodium salt of β -naphthol sulfonate formaldehyde condensate) vs. curing time. [Data from El-Hosiny F I; Gad E A M, *J. Appl. Polym. Sci.*, 56, No.2, 11th April 1995, p.153-9.]

cussed below, superplasticizers compete for the surface groups on cement grains. Plasticizers form irreversible bonds with grains therefore if both superplasticizer and plasticizer are used in the same formulation superplasticizer must be added first because it will not be able to replace plasticizer-grain bonds.

Superplasticizers are a class of materials which reduce viscosity and yield stress of the cementitious mixture. Superplasticizers have their sulfonic groups oriented towards water with their other side attached to cement grains. They form a monolayer around the grains. The water trapped within the original flocks is released and contributes to the mobility of concrete paste and its workability (reduced viscosity within certain time frame). Superplasticizers do not have much effect on surface tension of water.¹⁷⁵

Kinetics of hydration can be followed by estimating free lime. Figure 13.2 shows that control (without superplasticizer) has substantially more free lime than superplasticized composition.¹⁷³ This shows that superplasticizer decreased hydration by formation of a thin layer around particles of cement which affected the rate of liberation of free lime.¹⁷³ Figure 13.3 shows that substantially more water was used when concrete did not contain superplasticizer. Figure 13.4 shows that concrete is stronger when superplasticizer is incorporated.

13.5.6 EXAMPLES OF FORMULATIONS

Composition for prefabricated buildings:¹⁸²

Portland cement	40.3% wt%
Sand	40.3
Alkali resistant glass fibers	2.9
Acrylic polymer	4.0
Super plasticizer (e.g., Daracem 19)	0.4

Water	12.1
Spraying cementitious composition: ¹⁸⁴	
Standard sand	1800 parts
Portland cement	450
Water	200
Superplasticizer (Rheobuild 3520)	4.5
Acid-containing accelerator	18

13.6 COATED FABRICS

Large number of polymeric materials are involved in web coating. These include polyvinylchloride, polyurethanes (thermoplastic and thermoset; solvent-based and water-based), natural, nitrile, chloroprene, and ethylene-propylene rubbers, silicones, polyethylene (chlorinated and chlorosulfonated), polyamide, polyester, acrylic resins, polyvinylalcohol, polytetrafluoroethylene, and ethylene-vinyl acetate copolymer as the main matrices of polymer coatings.¹⁹³ Most of these polymers are not plasticized or seldom plasticized and these specific cases of plasticization are usually outlined in Chapter 11. Polyvinylchloride is a polymer which uses large quantities of plasticizers because most coatings are based on plastisols, and the ones that are not (calendering, hot roll coating, curtain coating, and extrusion coating) also use highly plasticized material.

Practically any plasticizer suitable for plasticization of polyvinylchloride is used in fabrication of coated materials because of their very diverse applications which require flexibility, broad range of service temperatures, abrasion resistance, high tensile strength, tear resistance, excellent adhesion to various substances, flame retarding properties, and chemical resistance each of which requires specific composition and thus plasticizers.¹⁷¹ The information given in the following sections reflects only the most recent trends based on current patents and publication and thus does not cover this big variety of technological processes and plasticizers traditionally used.

13.6.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) phthalate in armrest and headrest coated fabrics in railway,¹⁹⁵ in interpolymer compositions used in sound blocking and vibration damping,¹⁹⁹ and in water swellable coating²⁰⁰
- diisodecyl phthalate in geosynthetic material²⁰³
- C₇ to C₁₁ phthalate in mine brattice cloth²⁰¹
- di-(2-ethylhexyl) adipate in water swellable coating²⁰⁰ and in combination with benzoate plasticizer¹⁹⁸
- dipropylene glycol dibenzoate in leather imitation¹⁹⁸
- diethylene glycol dibenzoate in leather imitation¹⁹⁸
- triethylene glycol dibenzoate in leather imitation¹⁹⁸
- triphenyl phosphate in armrest and headrest coated fabrics in railway¹⁹⁵ and in mine brattice cloth²⁰¹
- octyl diphenyl phosphate in armrest and headrest coated fabrics in railway¹⁹⁵
- polyethylene glycol in antibacterial and antiviral coatings²⁰⁴
- epoxidized soybean oil^{198,201}

- biodegradable plasticizer in PVC coating which degrades in 60% after 28 days under ASTM D584 standard²⁰⁶

13.6.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: from 3 to 11 wt% in armrest and headrest coated fabrics in railway (total plasticizer from 8 to 24 wt%),¹⁹⁵ 0.5 to 25 wt% in interpolymer compositions used in sound blocking and vibration damping,¹⁹⁹ and 100 phr in water swellable coating²⁰⁰
- diisodecyl phthalate: 20 to 30 wt% of fiber glass based geosynthetics²⁰³
- di-(2-ethylhexyl) adipate: 100 phr in water swellable coating²⁰⁰
- triphenyl phosphate: from 1 to 5.4 wt% in armrest and headrest coated fabrics in railway (total plasticizer from 8 to 24 wt%)¹⁹⁵ and 39 phr in mine brattice cloth²⁰¹
- octyl diphenyl phosphate: from 2 to 4.5 wt% in armrest and headrest coated fabrics in railway (total plasticizer from 8 to 24 wt%)¹⁹⁵

13.6.3 REASONS FOR PLASTICIZER USE

- lowering of glass transition temperature¹⁹⁹
- lower fusion and gelation temperatures²⁰⁰
- changing polymer state from solid to liquid which opens new methods of processing¹⁹⁶
- increase of workability²⁰²
- increase of pliability²⁰²
- fire retardation properties²⁰¹
- modification of viscosity^{196,205}
- modification of rheological character of liquid¹⁹⁶
- helping in disappearance of boundaries between original PVC grains during fusion and gelation processes²⁰⁰
- improved stain resistance (benzoates)¹⁹⁸
- sound blocking¹⁹⁹
- vibration damping¹⁹⁹
- performs as an excipient (e.g. polyethylene glycol)²⁰⁴

13.6.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- some benzoates are highly solvating plasticizers useful in coated fabrics production¹⁹⁸

Disadvantages

- effect of temperature on plasticizer migration rate¹⁹⁵
- effect of contacting material (e.g., polyurethane foam) on plasticizer migration¹⁹⁵
- structural changes in material (formation of heterogeneities – e.g., non-filled domains) during use cause plasticizer migration¹⁹⁵
- some benzoates are less effective in viscosity modification¹⁹⁸
- cracking after some plasticizer was lost²⁰⁵

13.6.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Rheological properties of PVC pastes can be conveniently modelled by Ostwald-deWaele, power model:

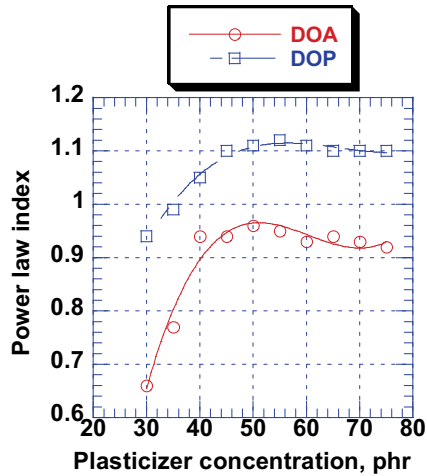


Figure 13.5. Power law index from eq 13.1 for PVC plastisols containing variable amounts of di-(2-ethylhexyl) phthalate, DOP, and di-(2-ethylhexyl) adipate. Emulsion PVC used had K value of 70. [Data from Zadhoush A; Alsharif M A, *J. Industrial Text.*, **30**, No.1, July 2000, p.50-62.]

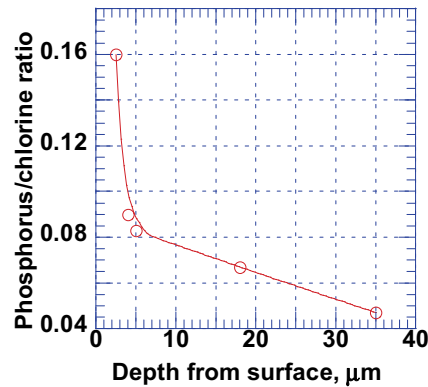


Figure 13.6. Depth profile of phosphorus/chlorine ratio of phosphoric plasticizer containing PVC coated fabric. The average concentration of phosphorus/chlorine ratio is 0.04. [Adapted, by permission, from Monney L; Jamois-Tasserie M; Dubois C; Villa F; Lallet P; Renaud C, *Polym. Deg. Stab.*, **72**, No.3, 2001, p.459-68.]

$$\mu = k\dot{\gamma}^{n-1} \quad [13.1]$$

where:

μ	apparent viscosity
k	consistency index
$\dot{\gamma}$	shear rate
n	power law index

Figure 13.5 shows that power law index for DOA increases rapidly in the beginning soon approaching unity. DOA forms plastisols which have pseudoplastic properties ($n < 1$) to Newtonian properties. In the case of DOP, below 50 phr there is also rapid increase in power law coefficient which soon becomes larger than unity. Higher additions of plasticizer induce slight shear thinning properties.¹⁹⁶

Figure 13.6 shows that there is always higher concentration of low molecular plasticizer on the surface which ultimately leads to plasticizer loss from the system. Studies of armrest and headrest fabrics showed that temperature aging only partially simulates real loss of plasticizer from material with other important parameters being structural, and perhaps chemical, changes in PVC, contact with other bodies (e.g., skin, hair, polyurethane foam), and cleaning.¹⁹⁵

13.6.6 EXAMPLES OF FORMULATIONS

General formulation of PVC coated fabric used by railways: ¹⁹⁵	
PVC	33-38 wt%
Plasticizers	20-23
Mineral fillers	25-30

Stabilizers	0.5-1
Polyamide fiber textile	13-15
Skin layer of PVC coated fabric: ¹⁹⁸	
PVC	100 parts
Plasticizer	65
Epoxidized soybean oil	5
Carboxylic acid derivative	5
CaCO ₃	15
Barium-zinc stabilizer	3
Foam layer of PVC coated fabric: ¹⁹⁸	
PVC	100 parts
Plasticizer	75
Epoxidized soybean oil	5
Azodicarbonamide	2
Zinc oxide	0.8
Barium-zinc stabilizer	1.5
TiO ₂	3
Mine brattice cloth: ²⁰¹	
PVC	100 parts
Triaryl phosphate	20-60
C ₇ -C ₁₁ phthalate	0-30
Chloroparaffin (Chlorowax 500)	0-30
Epoxidized soya oil	0-5
Antioxidant	0-2
Thermal stabilizer	1-5
Slip/antiblock agent	0-1
Lubricant/metal release agent	0-1
Toner	0-1

13.7 COMPOSITES

Bone/polyurethane composite contains general plasticizer, which is selected to produce product moldable at lower temperature and make liquid composite workable.^{207,209} Polyurethane is made out of biodegradable components but plasticizer can be general non-reactive plasticizer.^{207,209}

Citrate/lipid mixture is used as biodegradable plasticizer in biodegradable composite.²⁰⁸ The reason to use plasticizer is to prepare it in form which can be molded, calendared, or injection molded.²⁰⁸ Without plasticizer composite does not have sufficient fluidity.²⁰⁸ Citrate plasticizer is used to be compatible with polymer which is selected from biodegradable materials.²⁰⁸

Generally available plasticizers are used in composites containing nanofibers.²¹⁰ Plasticizers provide means of uniform distribution of nanofiber.²¹⁰

Plasticizers play by far more important role than can be anticipated from this review of available literature. Considering that composites contain fillers they require liquid additive which helps to form pliable mass which can be processed by any general method used in plastic industry.

13.8 COSMETICS

13.8.1 PLASTICIZER TYPES

- diisopropyl adipate in a cosmetic emulsion²³²
- diisobutyl adipate in hair composition²⁴⁰
- dioctyl adipate in radiation curable nail coating²¹⁴
- acetyl tributyl citrate in cosmetic films,²¹¹ in cosmetic pad for improving skin appearance,²¹⁷ and in nail varnish^{224,227,228}
- acetyl tri-(2-ethylhexyl) citrate in hair cosmetic composition²⁴⁰
- trioctyl dodecyl citrate in cosmetic films²¹¹
- triacetin in cosmetic films²¹¹
- diethyl phthalate²¹⁵
- dibutyl phthalate in nail polish²²¹ and in nail varnish²²⁹
- glyceryl stearate in composition containing tensioning agent²¹²
- glycerin in hair product²²⁰ and in anti-acne cosmetic composition²²⁵
- dipropylene glycol n-propyl ether²²¹ in nail varnish²²⁹
- dipropylene glycol in anti-acne cosmetic composition²²⁵ and color capsules²⁴⁶
- tripropylene glycol monoethyl ether in hair-setting composition²⁴³
- castor oil in smear resistant cosmetic^{213,226} and in lip cosmetic²⁴²
- polyethylene glycol in adhesive²¹⁸ and in color capsules²⁴⁶
- 1,3-butylene glycol²³⁴
- dibutyl maleate in film-forming composition²¹⁹
- dioctyl maleate in film-forming composition²¹⁹
- isopropyl-pareth-9-carboxylate (Velsan P8-3) in cosmetic gel composition²⁴¹
- polyester adipate (Paraplex G-50) in nail polish^{221,233}
- polyester sebacate (Paraplex G-25) in nail polish^{221,233}
- jojoba wax (PEG-80) in oil-free cosmetic composition²²²
- Veronia oil in nail varnish²⁴⁴
- 1,3-butanediol in color capsules²⁴⁶
- carbonate of natural origin in film forming composition²⁴⁷
- water-soluble plasticizer in eyeliner, mascara, and lipliner²⁴⁸
- esters of anhydrosugar alcohols in cosmetics²⁴⁹

13.8.2 PLASTICIZER CONCENTRATION

- dioctyl adipate: 10 to 30 wt% in radiation curable nail coating²¹⁴
- acetyl tributyl citrate: 5 wt% in composition for strengthening nails,²¹⁴ 10 wt% in skin permeation enhancer,²¹⁷ and 6 wt% in colored nail varnish²²⁷
- trioctyl dodecyl citrate: 44 wt% in moisturizing composition²¹¹
- triacetin: 4.7 wt% in topcoat of nail enamel²¹¹
- diethyl phthalate: 50 phr in cellulose acetate butyrate²¹⁵

- dibutyl phthalate: 1.6 to 3.9 wt% in addition to 10 wt% dipropylene glycol n-propyl ether in nail varnish²²⁹
- dipropylene glycol: 5 to 7 wt% in addition to 4 wt% of glycerin in anti-acne cosmetic composition²³⁵
- tripropylene glycol monoethyl ether: 20 wt% in hair-setting composition²⁴³
- glyceryl stearate: 3 wt% in anti-wrinkle cream²¹²
- jojoba wax (PEG-80): 9 wt% in oil-free composition²²²
- jojoba oil: 13 wt% in addition to 15 wt% of castor oil in lipstick formulation²³⁸

13.8.3 REASONS FOR PLASTICIZER USE

- decreasing of glass transition temperature^{217,225,238}
- improvement of mechanical properties^{212,237}
- improvement of impact resistance²⁴¹
- obtaining more flexible films^{215,218,219,223,224,228,244,248}
- increased resistance to rub-off²¹⁵
- enhancing film forming properties^{215,223}
- retaining cosmetically acceptable properties²¹²
- improvement of optical clarity²¹⁵
- preventing film from chipping from nails²¹⁹
- improvement of adhesion to keratin²³⁷
- permanence of effect²¹⁹
- low vapor pressure²⁴⁰

13.8.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- in some cases combination of two plasticizers (n-ethyl-o,p-toluenesulphonamide and tributyl acetyl citrate) gives good resistance to yellowing which will be inferior if only one plasticizer was used (n-ethyl-o,p-toluenesulphonamide) and gloss which will be inferior if only one plasticizer was used (tributyl acetyl citrate)²²³

Disadvantages

- excessive amount of plasticizer reduces holding ability of resin²²⁰
- some plasticizers may cause yellowing²²³
- addition of some plasticizers increases potential of heat aging²²³
- deterioration of gloss²²³
- some plasticizers form cloudy films²³¹
- some plasticizers change neutralization levels²³¹
- some plasticizers are lost by evaporation and migration causing change in properties^{240,245}
- use of phthalates because of potential for allergy²⁴⁴
- use of camphor because of its high volatility²⁴⁴

13.8.6 EXAMPLES OF FORMULATIONS

Anti-wrinkle cream:²¹²

Cetyl alcohol	4 wt%
Liquid petroleum jelly	8
Sorbitan tristearate	0.9
PEG-40 stearate	2

Glyceryl stearate	3
Plant oil	4
Cyclomethicone	5
Succinyl derivative of chitosan	7
Sancure 2060	20
Demineralized water	46.1

Hair conditioning solid:²²⁰

Water	25.6 wt%
Sodium stearate	7.0
PEG-6 caprylic/capric triglyceride	20.0
Sugar	6.0
Glycerin	20.0
Methyl paraben	0.1
PVP/VA copolymer	10.0
Ethanol	10.0
Fragrance	1.0
Germall II	0.3

A nail varnish:²²⁴

Nitrocellulose	16 parts
Acetyl tributyl citrate	6
Toluenesulphonamide formaldehyde resin	10
Bentonite clay	1.5
Pigments	1.5
Isopropyl alcohol	3
Recombinant spider silk protein	0.5
Solvents (ethyl acetate and butyl acetate)	100

Colored nail varnish:²²⁷

Nitrocellulose	20 wt%
Tributyl acetyl citrate	6
Toluenesulphonamide-formaldehyde resin	4
N-chlorosuccinimide	0.4
D&C Red No. 33	0.001
Other pigments and dyes	1
Solvents (ethyl acetate, butyl acetate, acetone 20/60/20)	68.599

A pearlescent nail varnish:²²⁸

Nitrocellulose	12 wt%
Alkyd resin	5
Tributyl acetyl citrate	3
Fluoroalkylsilicone	3
Isopropyl alcohol	8
Hectorite	1

Pearlescent pigments	0.5
Ethyl acetate/butyl acetate	67.5

13.9 CULTURAL HERITAGE

NIR chemical imaging was employed in 2D quantitative determination of plasticizers in heritage objects.²⁵⁰ Semiquantitative mapping of plasticizer distribution in plastic object can be obtained by the method used.²⁵⁰

13.10 DENTAL MATERIALS

13.10.1 PLASTICIZER TYPES

- dibutyl phthalate in tissue conditioners,²⁵¹ in microwave curable materials for dentures and prosthetics,²⁵⁵ in dental cements,²⁵⁶ in glass material for living tissue replacement,²⁵⁹ in restorative material,^{263,286} in dental cement for temporary prosthesis,³⁵⁴ in temporary crowns and bridges and delivery systems,²⁶⁸ in dental compositions,^{269,280,284} in fluoride releasing composite,²⁷⁵ in composition to treat fungal infections,^{277,279} and in compositions to treat gingivitis, and oral plaque, and in soft lining materials²⁸²
- diethyl phthalate in dentures²⁸³
- dioctyl phthalate in dental cements,²⁵⁶ in dental compositions,^{269,280} and in fluoride releasing composite²⁷⁵
- dinonyl phthalate in dental cements,²⁵⁶ in dental compositions,^{269,280} and in fluoride releasing composite²⁷⁵
- benzyl butyl phthalate in dental cement for temporary prosthesis²⁶⁴
- benzyl octyl phthalate in impression material^{270,273} and in polyvinylsiloxane impression material²⁷³
- butyl phthalyl butyl glycolate in temporary restorative resin²⁸⁶
- diisobutyl adipate in dental appliance²⁶⁵
- triethyl citrate in oral patch²⁶¹ and temporary restorative resin²⁸⁵
- acetyl tri-n-butyl citrate in tissue conditioners,²⁵¹ dentures²⁸³ and temporary restorative resins²⁸⁵
- di-butyl sebacate in temporary restorative resin²⁸⁵
- di-(2-ethylhexyl) maleate, a polymerizable plasticizer in denture lining material²⁵²
- glycerin in solid oral product for remineralizing subsurface dental lesions,^{254,278} in antimicrobial polishing compound,²⁶⁷ in sintering glass material for living tissue replacement,^{271,276} in restorative resin compound,²⁸⁸ in apparatus for whitening teeth²⁸⁹
- white oil in dental floss^{262,272}
- castor oil in apparatus for whitening teeth²⁸⁹
- polypropylene glycol (molecular weight 4,000 daltons) in temporary crowns and bridges and delivery systems²⁶⁸
- polyethylene glycol (molecular weight 4,000 daltons) in dental composition for hypersensitive teeth,²⁷⁴ (molecular weight of 400 daltons) in composition to treat

fungal infections,²⁷⁷ in compositions to treat gingivitis, oral plaque and fungal infections,²⁷⁹ and in restorative compound²⁸⁸

- terpolymer of ethylene, carbon monoxide, and butyl acrylate (Elvaloy HP441) in dental floss²⁶⁰
- propylene polymer having acrylic end-groups (Polybond 1002 or Orevac 9314) in dental floss²⁶⁰
- polybutyl methacrylate having molecular weight of 1000 to 10000 in tissue conditioner²⁸⁷
- silicone oil in restorative resin compound²⁸⁸

13.10.2 PLASTICIZER CONCENTRATION

- benzyl butyl phthalate: 37.5 phr in dental cement for temporary prosthesis²⁶⁴
- benzyl octyl phthalate: 4 to 5 wt% in impression material²⁷⁰ and 0.5 to 2 wt% in polyvinylsiloxane impression material²⁴⁰
- glycerin: 0.5 to 15 wt% in solid oral product for remineralizing subsurface dental lesions²⁵⁴ and 1 wt% in dental composition for hypersensitive teeth²⁷⁴
- polyethylene glycol (molecular weight 4,000 daltons): 1 wt% in dental composition for hypersensitive teeth²⁷⁴
- white oil: 125 phr in plasticization of Kraton copolymers for dental floss²⁶² and 0.1 to 1 wt% in dental floss²⁷²

13.10.3 REASONS FOR PLASTICIZER USE

- biocompatibility²⁵⁷
- expands rubber network²⁵⁸
- compatibility with matrix polymer²⁸¹
- increases release rate of active component when the amount of plasticizer increases^{277,279}
- to reduce melt viscosity^{260,273}
- viscosity regulation²⁷⁰
- obtaining thixotropic properties²⁷³
- to avoid or reduce crystallization²⁸¹
- to improve drawing characteristics of extruded monofilament²⁶⁰
- decrease of compression strength of polymer in restorative resin based on mono(meth)acrylate²⁸⁸

13.10.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- relatively cheap component^{258,281}
- no plasticizer bleedout²⁶²
- biodegradation by esterase²⁸²

Disadvantages

- migration^{227,237,282}
- sweating (forming droplets during curing at room temperature)²⁷⁰
- may influence water absorption undesirable in some applications²⁸¹
- may influence dimensional changes²⁸¹

13.11 ELECTRICAL AND ELECTRONICS

13.11.1 PLASTICIZER TYPES

- dibutyl phthalate in dielectric ceramic composition,²⁹⁴ in conductive roller,³³⁵ in circuit board,³³⁸ in production of zinc oxide varistor,³⁴¹ and in grounding electrode³⁵²
- dioctyl phthalate in dielectric ceramic composition,²⁹⁴ in photoreceptor,³¹³ in sintering of ceramic members,³³¹ in conductive roller,³³⁵ and in submount³³⁶
- butyl octyl phthalate in light transmitting device in presence of electric field³⁰⁵
- butyl phthalyl butyl glycolate (1,2-benzenedicarboxylic acid, 2-butoxy-2-oxoethyl butyl ester) in antenna element²⁹⁸ and in double layer capacitor^{310,320}
- benzyl butyl phthalate in multilayer capacitor³⁰⁹
- triisononyl trimellitate in low smoke composition³³⁰
- dioctyl sebacate in electrophotographic apparatus³⁰⁴
- phthalate plasticizer with attached UV absorber in coating of electrical and optical cables³⁵⁷
- dibutyl adipate in gel actuator³⁵⁴
- dibenzoate plasticizer in liquid electrical tape³⁵⁶
- tricresyl phosphate in electrode material³⁰³ and in conductive roller³³⁵
- triphenyl phosphate in photographic support material³²²
- mineral oil with low aromatic content (e.g., Isopar L) in twisting ball display,^{293,299,325,329,337,340} in tubular coverings for electric components,³⁰² in grommet,³⁰⁸ and in cable elastic sleeves³¹⁴
- naphthenic mineral oil in image forming device^{323,339}
- polyethylene glycol in dielectric ceramic composition²⁹⁴
- glycerin in double layer capacitor³¹¹ and in optical polarizer³⁵³
- polar plasticizer³⁵⁵
- chlorinated paraffin in electrophotographic receptor²⁹⁶
- adipic acid based polyester having molecular weight of 2320 daltons (Adecacizer PN150) in electrode-forming composition³⁰⁶
- conductive plasticizer (US-600-6) in conductive roller³⁰⁷
- polysiloxane oil in battery jar material³¹⁷

13.11.2 PLASTICIZER CONCENTRATION

- dibutyl phthalate: 2.5 wt% in production of zinc oxide varistor³⁴¹ and 9 to 10 wt% in grounding electrode³⁵²
- dioctyl phthalate: 3 to 5 wt% in sintered ceramic members³³¹ and 5 wt% in submount³³⁶
- benzyl butyl phthalate: 2 to 5 wt% in multilayer capacitor³⁰⁹
- butyl phthalyl butyl glycolate: 0.5 phr in electric double layer capacitor³²⁰
- dioctyl sebacate: 25 phr in plasticization of NBR used in charging roller³⁰⁴
- dibutyl adipate: 100-200 phr in gel actuator³⁵⁴
- polar plasticizer: 20-70 wt% in electroactive polymer composition³⁵⁵
- paraffinic oil: 25 phr in tubular coverings for electric components,³⁰⁵ 150 phr in grommet,³⁰⁸ and 40 phr in cable elastic sleeves³¹⁴

- naphthenic mineral oil: 35 phr in plasticization of NBR in image forming device^{323,339}
- polyethylene glycol: 0.1 to 5 wt% in dielectric ceramic composition²⁹⁴
- adipic acid based polyester having molecular weight of 2320 daltons (Adecacizer PN150): from 10 to 40 wt% in electrode-forming composition³⁰⁶

13.11.3 REASONS FOR PLASTICIZER USE

- dielectric properties^{293,325,329,337,340}
- viscosity regulation^{293,325,329,337,340}
- improves flow properties³⁰¹
- plasticizers improve blending of polymers²⁹¹
- improvement of processing²⁹¹
- facilitates mixing³⁰¹
- improvement of mechanical strength^{295,296}
- improvement of flexibility^{295,296,324,343,346,343}
- decreases hardness of roller^{316,348} and PU curable composition³²⁸
- improvement of film-forming properties²⁹⁵
- flame retarding properties³³²
- improves binding between particles of phosphor and matrix²⁹⁷
- actuation performance³⁵⁴
- electroactivity³⁵⁵
- swells matrix polymer making balls disposed in matrix to rotate^{293,334}
- capability to transport holes (selected plasticizers) important in photorefractive polymer systems²⁹²

13.11.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- plasticizers which have low loss of weight at elevated temperatures³²⁸
- plasticizers may increase printing sensitivity of dye receptor layer³¹⁸
- reduces amount of binder needed³²⁰
- gives fluidity to electrolyte^{333,345,350}
- ionic conductivity increases with plasticizer concentration increasing^{333,350}

Disadvantages

- inferior adhesion at low concentrations of plasticizer³⁰⁶
- gelation of electrode-forming composition³⁰⁶
- adversely affects electric double layer³⁰⁶
- resistance of roller changes with time when plasticizer is lost^{316,328}
- plasticizer may contaminate photosensitive^{316,324} or insulating medium³⁴⁶
- mechanical properties (e.g., hardness) are changed when plasticizer is lost^{316,328}
- sometimes transparency is affected³⁴²
- smoke generation during molding³⁴²
- influences characteristics of photoconductive layer³⁴⁷
- change in proportion of plasticizer and insecticide because of plasticizer and insecticide loss affects biological protection³⁵²
- bleeding^{324,328,342,346,347}

13.12 FIBERS

13.12.1 PLASTICIZER TYPES

- various phthalate and trimellitate plasticizers are suitable for PVC fiber³⁵⁸
- dibutyl phthalate in glass fiber sizing composition³⁷²
- triphenyl phosphate in cellulose diacetate³⁶⁵
- diethylene glycol dibenzoate in cellulose diacetate³⁶⁵
- glycerin in biodegradable fiber³⁶⁴ and in hemicellulose fiber³⁷⁴
- polyethylene glycol, sorbitol, xylitol, or mannitol in hemicellulose fiber³⁷⁴
- mineral oil in polypropylene based fibers^{373,375}
- polyester plasticizer in cellulose acetate fiber³⁶⁹

13.12.2 PLASTICIZER CONCENTRATION

- dibutyl phthalate: 3 to 5 wt% in sizing composition for glass fiber³⁷²
- triphenyl phosphate: 3 to 6 wt% in cellulose diacetate³⁶⁵
- diethylene glycol dibenzoate: 2 to 5 wt% in cellulose diacetate³⁶⁵
- glycerin: 2 wt% in biodegradable fiber³⁶⁴
- polyester plasticizer: 6.5 wt%³⁷⁰

13.12.3 REASONS FOR PLASTICIZER USE

- facilitates processing^{367,368}
- lowering melt viscosity³⁵⁸
- improves elasticity^{360,362,367,368,373}
- improves toughness^{360,362,367,368}
- increases dye uptake rate³⁷¹

13.13 FILM

13.13.1 PLASTICIZER TYPES

- dioctyl adipate in low temperature heat shrinkable film for labels³⁹⁷ and in transparent antiblocking film for food packaging⁴¹⁰
- diisononyl adipate in antibacterial film suitable for food packaging⁴¹²
- acetyl tributyl citrate in protecting film for skin,³⁹² in biodegradable lactide film,³⁵⁶ and in film with controlled gas permeability^{406,423}
- dibutyl phthalate in solder resist film,³⁸⁵ in shrink film,³⁹⁹ in base film for conductive or magnetic layer,⁴⁰³ in polyethylene microporous film obtained by plasticizer extraction,⁴⁰⁷ in transparent antiblocking film for food packaging,⁴¹⁰ and in photographic film base⁴²⁵
- di-(2-ethylhexyl) phthalate in packaging films,³⁷⁸ in agricultural film with infrared absorber,³⁸⁷ in piezoelectric film,³⁹⁸ in shrink film,³⁹⁹ in anisotropic, conductive film,⁴⁰¹ in base film for conductive or magnetic layer,⁴⁰³ and in polyethylene microporous film obtained by plasticizer extraction⁴⁰⁷
- triphenyl phosphate in cellulose acetate film for optical compensation of liquid crystal display,³⁸³ in UV absorbing film for protection of liquid crystal display,^{404,420} in protective film for polarizing plate,⁴¹⁵ and in photographic film base⁴²⁵

- tricresyl phosphate in agricultural film with infrared absorber,³⁸⁷ in anisotropic, conductive film,⁴⁰¹ and in protective film of polarizing plate⁴⁰⁹
- tri-(2-ethylhexyl) trimellitate and dtridecyl phthalate are low vapor pressure plasticizers useful in materials processed by vacuum deposition⁴³⁵
- cyclohexane dicarboxylate in protective film⁴³⁶
- carbonate plasticizers in electrochromic materials
- polypropylene glycol (molecular weight 2,000 daltons) in breathable film³⁸⁶
- castor oil in breathable film³⁸⁶
- glycerin in agricultural film with infrared absorber,⁴⁰⁰ in water soluble film,⁴⁰⁵ in edible film based on a blend of protein and polysaccharide,⁴¹¹ and in high barrier film based on polyamide⁴³⁰
- glyceryl monostearate in polyester shrink film⁴¹⁹
- epoxidized soybean oil in film with controlled gas permeability,⁴⁰⁶ in polyvinylidenechloride film,⁴¹⁴ in barrier blend for food packaging,⁴¹⁸ and in food-packaging film⁴³³
- epoxidized linseed oil in antibacterial film suitable for food packaging⁴¹²
- paraffin oil in display film³⁹¹
- polyester plasticizer in acrylic film³⁹⁶
- tripropylene glycol methyl ether in poly(methyl vinyl ether-co-maleic anhydride) bioadhesive film⁴³⁴

13.13.2 PLASTICIZER CONCENTRATION

- dioctyl adipate: 6 to 6.5 wt% in low temperature heat shrinkable film³⁹⁷
- diisononyl adipate: 20 phr (in addition to 10 phr of epoxidized linseed oil) in antibacterial film suitable for food packaging⁴¹²
- acetyl tributyl citrate: 0.5 to 2 wt% in skin protecting film,³⁹² 5 to 25 wt% in lactide biodegradable film,⁴⁰⁴ or 8 to 10 wt% in polyvinylidenechloride film having controlled gas permeability⁴²³
- dibutyl phthalate: 13 to 17 wt% in photographic film base⁴²⁵
- di-(2-ethylhexyl) phthalate: 30 wt% (in addition to 3 wt% of tricresyl phosphate) in agricultural film with infrared absorber,³⁸⁷ 4.5 wt% in piezoelectric film,³⁹⁸ or up to 3 wt% in shrink film³⁹⁹
- triphenyl phosphate: 11 phr in optical film,³⁸³ 5 to 15 wt% in UV absorbing film,³⁸⁴ 12 wt% in UV absorbing film,⁴²⁰ or 13 to 17 wt% in photographic film base⁴²⁵
- glycerin: 20 wt% in water soluble film based on polyvinylalcohol,⁴⁰⁵ 20 to 40 wt% in edible film based on a blend of protein and polysaccharide,⁴¹¹ or up to 10 wt% in high barrier film from polyamide⁴³⁰
- glyceryl monostearate: 2 to 6 wt% in polyester shrink film⁴¹⁹
- epoxidized soybean oil: 4 wt% in barrier blend for food packaging having increase permeability to CO₂³⁷⁰ and 1 to 5 wt% in food-packaging film⁴³³
- epoxidized linseed oil: 10 phr in antibacterial film suitable for food packaging⁴¹²

13.13.3 REASONS FOR PLASTICIZER USE

- decrease of glass transition temperature^{422,431}
- reduction melt viscosity⁴⁰⁴

- increases flexibility and reduces tendency to cracking⁴⁰⁴
- improvement in tear resistance and impact resistance⁴⁰⁴
- dielectric properties (e.g., paraffin oil)³⁹¹
- increased flexibility of film³⁹²
- increased drying speed^{417,424}
- easier extrusion and better orientation⁴²¹
- giving transparent film³⁹⁸
- fine control over shrinking temperature³⁹⁹
- lowers shrinking temperature of polyester film⁴³¹
- lowers thermoforming temperature of polysulfone film and improves stretching characteristics⁴²⁹
- increases mobility of photopolymerizable compound and thus photopolymerization rate³⁸¹
- applicable to breathable compounds (usually plasticizers which contain low reactivity oxygen linkages)³⁸⁶
- increases bonding between the phosphor and binder in radiographic films³⁸⁸
- biodegradability⁴⁰⁴
- low volatility⁴⁰⁴

13.13.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- plasticization of polyvinylidene chloride increases CO₂ permeability as required in cheese packaging (at the same time permeability of O₂ is also increased which reduces shelf life of cheese)^{394,418}
- solubility in solvent which does not affect matrix polymer in production of microporous films
- moisture absorbed acts like plasticizer⁴²⁷

Disadvantages

- transfer to the surrounding medium (e.g., food)³⁷⁸
- plasticizers from film migrate into adhesive and degrade its functionality³⁸⁹
- spotty film appearance due to plasticizer migration (sometimes referred to as mottle). This is most frequent problem in warm weather climates³⁸⁹
- migration of DOP from materials used for medical applications³⁹⁰
- plasticization may adversely affect optical properties of film³⁹⁴
- in multilayer material plasticizer migration may reduce adhesion between layers⁴⁰²
- migration of plasticizer in multilayer films may cause wrinkling by changing properties of adjacent films⁴⁰²
- increase in plasticizer concentration parallels increase in oxygen permeability which is undesirable in food packaging⁴²¹

13.14 FOOD

Several aspects are involved in relationship of plasticizer and food. These include: use of plasticizers in food preparation, plasticizer transfer to food from external sources (packaging or equipment), and the use of plasticizer in production of packaging materials and

other material in contact. The last subject was discussed in Section 13.13 but some additional information can also be found in this section. The two remaining subjects are discussed here based on information available in open literature³⁸⁶⁻⁴⁰¹ and in patents.⁴⁰²⁻⁴²⁹

13.14.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) adipate in cling films,⁴³⁹ plastic containers⁴⁸² and gaskets⁴⁸⁴
- di-(2-ethylhexyl) phthalate in cling films,⁴³⁹ in foamed gasket,⁴⁷⁵ and plastic containers⁴⁸²
- dimethyl phthalate in plastic containers⁴⁸²
- dibutyl phthalate in plastic containers⁴⁸²
- benzyl butyl phthalate in plastic containers⁴⁸²
- dibutyl sebacate in low temperature applications⁴⁴⁰ and gaskets⁴⁸⁴
- acetyl tributyl citrate in gaskets⁴⁸⁴
- dipropylene glycol dibenzoate in food packaging adhesive⁴⁵⁴
- polyethylene glycol having molecular weight of 3,000 daltons in coating of nutritional supplements, pharmaceuticals, etc.,⁴⁵⁵ in melt extruded pharmaceutical composition,⁴⁵⁸ in tablet coating (molecular weight 400 daltons),⁴⁶² in starch-based sheets (molecular weight below 600),⁴⁶⁸ and in starch-based containers⁴⁷⁶
- polypropylene glycol in flexible dough composition⁴⁶³
- glycerin in tablet coating,^{455,462} in edible film,⁴⁵⁶ in composition reducing risk factor during exercise,⁴⁵⁹ in modification of texture of food product,⁴⁶⁶ in starch-based sheets,⁴⁶⁸ in chewing gum product,⁴⁷⁰ in modification of texture by adding immobilized plasticizer slowly released during storage,⁴⁷² in fat-free composition,⁴⁷³ in tubular food casing^{474,480} in starch-based containers,⁴⁷⁶ and in gel products⁴⁸¹
- sorbitol in edible film based on casein,⁴⁵⁷ in composition reducing risk factor during exercise,⁴⁵⁹ in starch-based sheets,⁴⁶⁸ and in modification of texture by adding immobilized plasticizer slowly released during storage⁴⁷²
- lecithin in chewing gum product⁴⁷⁰
- poly(1,3-butylene adipate) in food packaging^{439,440}
- distilled acetylated monoglyceride (Eastman EPZ) suitable for direct and indirect contact with food⁴⁵¹
- fatty acid esters of polyglycerin as food plasticizers⁴⁶¹
- epoxidized soybean oil in lids⁴⁸³
- phospholipids in encased food product⁴⁸⁵
- polysaccharides and polyhydric alcohol in gloss coatings for food⁴⁸⁶

13.14.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 35 wt% in foamed gasket for food application⁴⁸⁴
- dipropylene glycol dibenzoate: 3 to 7.5 wt% in food packaging adhesive⁴⁵⁴
- polyethylene glycol having molecular weight of 3,000 daltons: 12 wt% in coating of nutritional supplements, pharmaceuticals, etc.,⁴⁵⁵ up to 5 wt% in pharmaceutical composition of lipid lowering agent,⁴⁵⁸ and 10 wt% of polyethylene glycol having molecular weight of 400 daltons in film coating system⁴⁶²
- polypropylene glycol: 12 to 14 wt% in flexible dough composition⁴⁶³

- glycerin: 5 wt% in coating of nutritional supplements, pharmaceuticals, etc.,⁴⁵⁵ 4 to 8 wt% in edible films based on casein,⁴⁵⁶ 10 wt% in film coating system,⁴⁶² 6 wt% in flexible dough composition,⁴⁶³ 1 to 2 wt% in food product containing encapsulated plasticizer,⁴⁶⁶ 20 wt% in fat free composition,⁴⁷³ and 8 wt% in film coating of nutritional products⁴⁷⁸

13.14.3 REASONS FOR PLASTICIZER USE

- lowering glass transition temperature⁴⁵⁵
- reduction in brittleness of polymer^{455,465}
- increase in flexibility^{463,465,468,481}
- improvement of mechanical properties⁴⁵⁷
- to counteract hardening of food⁴⁷²
- to prolong food's shelf life⁴⁷²
- to reduce polymer crystallization^{474,480}
- facilitate processing by extrusion and injection molding⁴⁵⁷
- facilitate thermoplastic properties⁴⁶⁵
- edible (e.g., glycerol, mannitol, sorbitol, maltitol, gum arabic, etc.)^{457,467,472}
- pharmaceutically acceptable (e.g., polyethylene glycol, ethylene glycol, polypropylene glycol, propylene glycol, etc.)⁴⁵⁸
- biodegradable (e.g., acetyl tributyl citrate, triacetin, dibutyl sebacate, triethylene glycol diacetate)^{460,464}
- increases water solubility (e.g., glycerin)⁴⁵⁷
- performs also as humectant (e.g., glycerin or propylene glycol)^{469,476,479}
- does not exude or bleed at elevated temperatures (e.g., 60 to 120°C)⁴⁶⁴

13.14.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- polymeric plasticizers slow down migration, extraction, and volatility⁴⁴⁰
- polymeric plasticizers having molecular weight above 1,000 daltons require less research before being approved for food contact by European Union because Scientific Committee for Food considers that there is little absorption in gastrointestinal tract, therefore no toxicological data are required⁴³⁸
- epoxidized soybean oil has widespread acceptance for food contact applications⁴⁴⁰

Disadvantages

- large distribution of molecular weights in polymeric plasticizers consists disadvantage in polymeric plasticizers because fractions below 1,000 daltons have to be subjected to relevant safety evaluation (toxicological data)⁴³⁸
- hydrolysis of plasticizer in digestive fluids requires studies on the toxicological effect of the products of hydrolysis⁴³⁸
- migration rate of plasticizer is an important factor in determining toxicological effect of plasticizer by European Union (if migration rate is below 5 mg/kg of food and substance is not mutagenic, a reduced toxicological information is required)⁴³⁸
- low molecular plasticizers, such as di-(2-ethylhexyl) adipate and di-(2-ethylhexyl) phthalate readily migrate to food^{439,443}

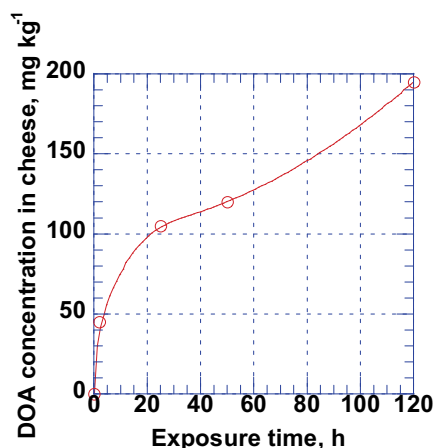


Figure 13.7. Concentration of di-(2-ethylhexyl) adipate in Danbo cheese wrapped in cling film and stored at 21°C vs. time from wrapping. [Data from Petersen J H; Naamansen E T; Nielsen P A, *Food Additives Contaminants*, 12, No.2, March/April 1995, p.245-53.]

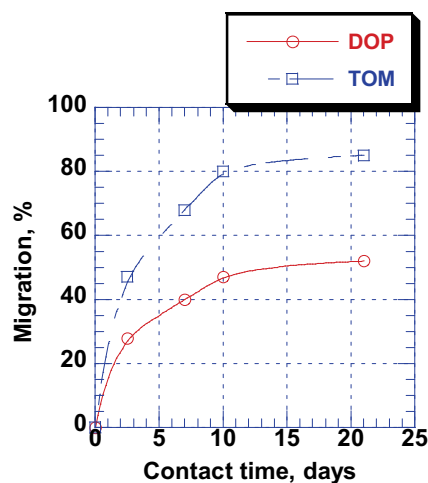


Figure 13.8. Migration of plasticizer from PVC into sunflower oil at 40°C. DOP – di-(2-ethylhexyl) phthalate, TOM – tri-(2-ethylhexyl) trimellitate. [Adapted, by permission, from Hamdani M; Feigenbaum A, *Food Additives Contaminants*, 13, No.6, Aug/Sept. 1996, p.717-30.]

- increased tackiness⁴⁵⁵

13.14.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Two methods are used to monitor concentration and restrict excessive use of polymer additives in contact with food: quantity in the materials and specific migration limit.⁴⁴³ If compound degrades in food simulant the quantity in the material should be used. From this follows that determination of stability of additives is important to establish which parameter has to be controlled. Low molecular weight plasticizers, such as di-(2-ethylhexyl) adipate and di-(2-ethylhexyl) phthalate are known to migrate into food in the contact. Their studies in various food simulants show that both materials are fairly stable and thus the quantity in the material is postulated to be used in screening of packaging materials.⁴⁴³

Selection of simulants is essential process. Different simulants give substantially different readings as was observed in studies on DOP migration using isopropanol and isooctane.⁴⁴⁶ Isopropanol always gave higher results than isooctane which is not surprising considering that diffusion process is mutual and thus isopropanol as a smaller molecule penetrates plasticized polymer with a higher rate.⁴⁴⁶

Various types of baby food were tested for presence and concentration of epoxidized soybean oil which was used in production of PVC gaskets used in lids for glass jars used for packaging.⁴⁴⁷ Highly variable amounts were found in different types of baby food ranging from less than 1.5 to 50.8 mg/kg of baby food. The mean value was 11.9 mg/kg. Assuming consumption of two portions of 135 g each per day gives daily intake of 3.2 mg of epoxidized soybean oil per day per child. With average child weight of 8.5 kg, daily intake is 0.38 mg per kg of body. This about three times lower than tolerable daily intake

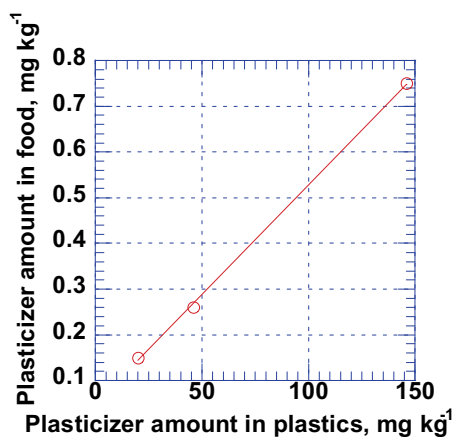


Figure 13.9. Amount of diisopropyl naphthalene in rice vs. its amount in cardboard after 60 days of storage. [Data from Boccacci Mariani M, Chiacchierini E, Gesmundo C, *Food Additives Contaminants*, **16**, No.5, 1999, p.207-213.]

of 1 mg/kg body proposed by Scientific Committee for Food of European Union.⁴⁴⁷

A study of daily intake of di-(2-ethylhexyl) adipate conducted in 1987 in UK estimated maximum intake at 16 mg/day.⁴⁴⁸ Similar studies conducted five years later gave maximum intake of di-(2-ethylhexyl) adipate at 8.2 mg/day. This was achieved by product reformulation with special attention given to cling film. The intake of acetyl tributyl citrate was found to increase because of usage of vinylidene chloride copolymer in microwave ovens.⁴⁴⁸

Studies of hydrolytic stability of polymeric plasticizers, such as poly(propylene adipate) and poly(butylene adipate) were conducted in simulated body fluids such as saliva, gastric and intestinal fluids.⁴³⁸ It was found that no hydrolysis occurred under

saliva and gastric conditions but plasticizers were hydrolyzed to a large extent in simulated intestinal fluid. Enzymes selectively catalyzed the primary alcohol ester linkage. It is expected that other polymeric ester plasticizers will behave in similar manner.⁴³⁸

Figure 13.7 shows migration of di-(2-ethylhexyl) adipate into cling film wrapped around Danbo cheese. After only five days concentration of DOA is about 195 mg/kg of cheese, meaning that average person needs to eat approximately 300 g of this cheese to have intake of DOA higher than 1 mg/kg body proposed by Scientific Committee for Food of European Union. Figure 13.7 also shows that migration of DOA after five days does not give any signs of slowing down.⁴⁵³

Figure 13.8 shows dependence of the migration rate of plasticizer from PVC into sunflower oil on chemical structure of plasticizer. The rate of migration depends on plasticizer and food simulant. For example, DOP had very similar rate of migration into three tested simulants (sunflower oil, isooctane, and ethanol). Migration of TOM into sunflower oil was shown already as faster than DOP but it is still slower than its migration into isooctane. Compatibilities of plasticizer, extractant, and matrix polymer affect rate of migration.⁴⁴⁹

Figure 13.9 shows that concentration of plasticizer in plastic material has linear influence over the rate and extent of plasticizer migration into food.

13.14.6 EXAMPLES OF FORMULATIONS

Coating of nutritional supplement tablets:⁴⁰³

Polyvinylalcohol	47.65 wt%
Talc	19.67
Soya lecithin	6.33
Glycerin	5.35
TiO ₂	2.31
FD&C Red 40 Lake	15.08

FD&C Yellow 6 Lake	3.41
FD&C Blue 2 Lake	0.20

13.15 FLOORING

13.15.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) adipate in welded seam maintains ease of cutting⁴⁹⁶
- butyl benzyl phthalate^{487,500} in covering underlayment⁵⁰¹
- di-(2-ethylhexyl) phthalate,^{494,497} in covering underlayment,⁵⁰¹ and in wiring flooring⁵⁰²
- oligomeric ester of phthalic acid and aliphatic dicarboxylic acid⁵⁴⁹
- dipropylene glycol dibenzoate^{487,550}
- C9 to C12 alkyl benzoate in PVC composition⁵⁰³
- 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (Kodaflex TXIB or Texanol isobutyrate) in carpet backing⁴⁹¹ and in covering underlayment⁵⁰¹
- epoxidized soybean oil in covering underlayment⁵⁰¹ and floor covering⁵⁰²
- esterified and epoxidized soybean oil^{502,505}
- epoxidized methyl soyate⁵⁰⁴
- sulfonamide-based or dicarboxylic acid based plasticizer in microcellular polyamide foam⁵⁵¹

13.15.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 10 to 30 phr^{494,497} and 88 phr in flooring for wiring⁵⁰²
- 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (Kodaflex TXIB): 8 to 12 wt% in carpet backing⁴⁹¹

13.15.3 REASONS FOR PLASTICIZER USE

- decrease in glass transition temperature⁵⁰⁰
- excellent compatibility with polymer^{488,490,491}
- flame retarding properties⁵⁰⁰
- lower viscosity⁵⁵²
- low temperature flexibility⁵⁰⁰
- improved adhesion⁵⁰⁰
- microbiological resistance⁴⁸⁸
- suitable for calendaring⁴⁹⁴

13.15.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- alkyl benzyl phthalates because of their high Small's solubility parameter give better staining protection than dialkyl phthalates⁴⁹⁸
- use of similar plasticizing systems and concentrations to minimize migration between layers⁴⁹⁶

Disadvantages

- plasticizers affect stain resistance^{488,499}

13.15.5 EXAMPLES OF FORMULATIONS

European basic topcoat formulation:⁴⁸⁷

PVC	100 parts
Plasticizer	44
Tin stabilizer	1.4
Epoxidized soybean oil	2.4

Floor covering underlayment:⁵⁰¹

PVC blending resin	40.0 parts
PVC dispersion resin	60.0
Limestone	70.0
ZnO, blowing agent initiator	0.5
Blowing agent (Kempore AF)	2.0
Epoxidized soybean oil	1.5
Texanol isobutyrate	7.0
Di-(2-ethylhexyl) phthalate	10.0
Butyl benzyl phthalate	25.0
Stabilizer (fatty acid salt)	4.0
Hydrocarbon solvent	5.0

13.16 FOAMS

13.16.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) phthalate in PVC foam,^{507,513} in interior automotive material,⁵¹² in polyurethane composition,⁵¹⁴ in PVC carpet backing,⁵²⁰ in automotive interior trim articles,⁵³⁶ and in polyurethane sealant⁵³⁸
- diisodecyl phthalate in polyurethane composition containing antimicrobial agents⁵²³
- diisononyl phthalate in cushioned carpet⁵⁰⁸
- C₇ to C₁₁ phthalate (Palatinol 711) in polyurethane prepolymer⁵⁴¹
- benzyl butyl phthalate in polyurethane composition⁵¹⁴
- diisooctyl adipate in shaped foam implements,⁵¹⁶ in microporous foam,^{521,523} in polyurethane sealant,⁵³⁸ in heterogeneous foam,⁵³⁹ and in thermal insulation⁵⁴⁴
- diisooctyl azelate in shaped foam implements,⁵¹⁶ in microporous foam,^{531,533} in heterogeneous foam,⁵³⁹ and in thermal insulation⁵⁴⁴
- diisooctyl sebacate in shaped foam implements,⁵¹⁶ in microporous foam,^{531,533} in heterogeneous foam,⁵³⁹ in thermal insulation,⁵⁴⁴ and in waterproof plastic foam⁵⁴⁸
- trioctyl trimellitate in automotive interior trim articles⁵³⁶
- 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (Texanol isobutyrate) in PVC foam,^{507,513} in polyurethane composition,^{511,524} and in frothing foam PU adhesive⁵³⁴
- 2-ethylhexyl diphenyl phosphate in extrudable composition⁵³⁵ and in polyurethane foams⁵⁴⁵
- isodecyl diphenyl in polyurethane foams⁵⁴⁵

- tricresyl phosphate in waterproof plastic foam⁵⁴⁸
- polyethylene glycol in biodegradable cellulose acetate foam⁵²⁷
- glycerin in polysaccharide foam⁵⁴⁰ and in starch polymer⁵⁴³
- sorbitol in starch polymer⁵⁴³
- paraffinic oil in rubber composition,⁵¹⁰ in molded synthetic composition,⁵¹⁸ in extruded product,⁵²⁰ in resilient cushion,⁵²² in ethylene α -olefin,⁵³⁷ and in polystyrene composition⁵⁴⁷
- epoxidized soybean oil in self-adhesive PVC gasket⁵²⁹ and in PVC composition⁵⁴²
- glutarate ester polymeric plasticizer (P550 by C. P. Hall) in low fogging vinyl foam⁵²⁶
- adipate ester polymeric plasticizer (RX13290 by C. P. Hall) in low fogging vinyl foam⁵²⁶

13.16.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 55 phr in addition to 5 phr of Texanol isobutyrate in PVC foam,^{507,513} 40 wt% in interior automotive material,⁵¹² and 60 to 100 phr in carpet backing⁵³⁰
- diisononyl phthalate: 5 to 15 phr in cushioned carpet⁵⁰⁸
- 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (Texanol isobutyrate): 5 to 10 wt% in polyurethane composition⁵¹¹
- polyethylene glycol: up to 50 phr in biodegradable cellulose acetate foam⁵²⁷
- paraffinic oil: 20 phr in natural rubber composition⁵¹⁰
- low molecular weight polystyrene in polystyrene foam⁵²⁵

13.16.3 REASONS FOR PLASTICIZER USE

- reduces viscosity and enhances flow properties^{524,541}
- facilitates processing⁵²⁰
- improvement of extrudability⁵³⁷
- induces hydrophobic properties⁵²⁴
- prevents crystallization of isocyanate⁵²⁴
- improves polyaddition process⁵⁴¹
- compatible with tackifier⁵³⁷

13.16.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- dispersion of antimicrobial agent in plasticizer is expected to encapsulate it and isolate from reacting with catalyst⁵²³

Disadvantages

- migration of plasticizer may cause adhesion problems with paint in steering wheel rims⁵¹⁷
- migrating plasticizer is absorbed in cushion and wrap material causing wrap to soften and degrade⁵¹⁷
- bleeding plasticizer tends to migrate into adhesive layer and degrade its properties⁵²⁹
- plasticizer may leach out of a polymer blend leading to degradation of its physical properties^{517,528}

13.16.5 EXAMPLES OF FORMULATIONS

Whitened polyvinylchloride foam:⁵⁰⁷

PVC dispersion resin	70 parts
PVC blending resin	30
DOP	55
TiO ₂ (whitener)	5
CaCO ₃	25
Azodicarbonamide (blowing agent)	2
Zinc oxide (activator)	0.05
Texanol isobutyrate	5

Carpet cushioning:⁵⁰⁸

Rubber (NBR)	50 parts
Additive rubber (EPDM)	50
Diisononyl phthalate	15
Trinonyl phenol phosphate (stabilizer)	2
Processing aid (Vanfree AP-2)	1.75
Octamine (antioxidant)	1.2
Sulfur	1.5
Stearic acid	1.2
Carbon black N-550	48
Vulkacit Thorium MS	0.6
Zinc oxide	6
Blowing agent	3

13.17 FOOTWEAR

13.17.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) phthalate as hydrophobic plasticizer in sustained gas release device,⁵⁶⁰ in foot massaging shoe insole,⁵⁶³ and in rubber composition⁵⁶⁴
- diisooctyl phthalate in synthetic rawhide lace⁵⁵⁷ and in foot massaging shoe insole⁵⁶³
- phthalate plasticizer in polyurethane gel, which plays a role of shock absorber⁵⁷⁴
- benzyl butyl phthalate in cushioning device⁵⁵⁶ and in shoe insert⁵⁵⁹
- tricresyl phosphate in foot massaging shoe insole⁵⁶³
- dipropylene glycol dibenzoate in conforming shoe composition^{569,573}
- chlorinated paraffin in shock absorbing footwear⁵⁶⁴
- naphthenic oil in shock absorbing footwear⁵⁶⁴
- paraffin oil in gel for protection against extreme cold weather,⁵⁵⁸ in conforming shoe composition,^{569,573} and in medial pad of skateboard shoe⁵⁷⁵
- process oil in floatable footwear⁵⁵³ and in microporous polyolefin for absorbing sweat⁵⁶⁶
- polytetramethylene ether glycol (Terathane 2000) in breathable film⁵⁵⁵
- N-ethyl o/p-toluene sulfonamide in footwear adhesive⁵⁷¹
- adipic acid polymer diol (Uniflex 314) in breathable film⁵⁵⁵

- epoxidized soybean oil in custom-fitting footwear⁵⁷²

13.17.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 80 phr in foot massaging shoe insole⁵⁶³ and 10 wt% in rubber composition⁵⁶⁴
- diisooctyl phthalate: 20 to 25 wt% in synthetic rawhide lace⁵⁵⁷ and 80 phr in foot massaging shoe insole⁵⁶³
- benzyl butyl phthalate: up to 5 wt% in cushioning device⁵⁵⁶ and 8 to 12 wt% in shoe insert⁵⁵⁹
- process oil: 6 vol% in microporous polyolefin for absorbing sweat⁵⁶⁶

13.17.3 REASONS FOR PLASTICIZER USE

- improvement of miscibility of formulation components⁵⁶⁰
- improvement of processing⁵⁵⁶
- improvement in flexibility of final product⁵⁵⁶
- modification of blend morphology⁵⁶⁰
- dispersion of catalyst⁵⁶⁷⁶
- increasing acid release property⁵⁷⁰

13.17.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- plasticizers used in breathable composition should contain sufficient number of ether, hydroxyl, and/or polyol linkages⁵⁵⁵

13.18 FUEL CELLS

13.18.1 PLASTICIZER TYPES

- dibutyl phthalate or butyl phenyl phthalate in green sheet of textured electrolyte sheet for fuel cell device⁵⁷⁶ and dibutyl phthalate in solid oxide fuel cell⁵⁷⁸
- polyethylene glycol in electrolyte membrane for fuel cell⁵⁷⁷

13.18.2 PLASTICIZER CONCENTRATION

- 20-200 phr polyethylene glycol in electrolyte membrane for fuel cell⁵⁷⁷

13.18.3 REASONS FOR PLASTICIZER USE

- lowering of glass transition temperature⁵⁷⁶
- improves plasticity⁵⁷⁶

13.19 GASKETS

13.19.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) phthalate in aerobically hardenable composition,⁵⁸¹ in hotmelt gasket,⁵⁸⁹ and in sanitary pipe fittings⁶⁰⁰
- diisodecyl phthalate in gaskets for clean rooms⁵⁸³
- di-(2-ethylhexyl) sebacate in gaskets for clean rooms⁵⁸³
- epoxidized soybean oil in oxygen scavenging seal composition^{580,582} and in gaskets for clean rooms⁵⁸³
- chlorinated paraffin in gaskets for clean rooms⁵⁸³

- ethylene glycol in aerobically hardenable composition⁵⁸¹
- paraffin oil in gasket for medical device⁵⁸⁸
- naphthenic oil in gasket for medical device⁵⁸⁸
- polymeric plasticizer (Huels 910) in low mar gasket⁵⁸⁴ and in liquid gasket for in-place forming⁵⁹²

13.19.2 PLASTICIZER CONCENTRATION

- polymeric plasticizer (Huels 910): 67 phr in low mar gasket⁵⁸⁴
- process oil, paraffin oil, dibutyl phthalate, dioctyl phthalate, dioctyl adipate, or dioctyl sebacate: 20-80 phr (EPDM) in hard disc drive gasket⁵⁹¹

13.19.3 REASONS FOR PLASTICIZER USE

- increase flexibility of material^{580,582}
- increase toughness of final product^{580,582}
- regulation of material hardness^{586,588}
- dispersion of active component^{580,582}
- low marring of pre-painted surface⁵⁸⁴

13.19.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- gaskets for clean rooms should have low emission of low molecular weight components. It was discovered⁵⁸³ that plasticizer having molecular weight above 400 daltons are not detected in air in a clean room. Lower molecular weight plasticizers, such as dibutyl phthalate (molecular weight of 278 daltons), di-(2-ethylhexyl) phthalate (molecular weight of 391 daltons) or di-(2-ethylhexyl) adipate (molecular weight of 371 daltons) are not suitable for this application.

Disadvantages

- plasticizer loss after curing⁵⁸¹
- substantial amounts of extractable materials (e.g. plasticizers) in gasket for blood sensor⁵⁸⁵

13.19.5 EXAMPLES OF FORMULATIONS

Low mar gasket:⁵⁸⁴

Geon 31 PVC resin	75.00 parts
Geon 3400 PVC resin	25.00
Epoxidized soybean oil	16.77
Huels 910 (polymeric plasticizer)	67.18
Calcium carbonate	50.00
Witco zinc complex stabilizer	1.50
Morton Thiokol fungicide (SB-1)	1.45
Color pigments	5.53

Gasket for sanitary pipe fittings:⁵⁹⁰

Butadiene-acrylonitrile copolymer	100.0 parts
Carbon black N550	27.0
Silica (powder)	45.0
Aluminum silicate	60.0

Silica (granular)	30.0
Dioctyl phthalate	5.0-10.0
Polyethylene powder	2.0-5.0
Zinc oxide	5.0-7.0
Stearic acid	1.0
Cotton flock	1.0-10.0
Sulfur	1.5-2.0
2-Mercaptobenzothiazol disulfide	2.0
Tetramethylthiuram monosulfide	1.5

13.20 HOUSEHOLD PRODUCTS

Di-(2-ethylhexyl) phthalate, di-n-butyl phthalate, butyl benzyl phthalate, diisononyl phthalate, di-n-octyl phthalate, diisodecyl phthalate, di-(2-ethylhexyl) adipate, 2,2,4-trimethyl-1,3-pentanediol diisobutylate, and mono 2-ethylhexyl phthalate in polyvinylchloride household products were analyzed.⁵⁹³ Concentration of these products were in range from 0.021 to 48 wt%.⁵⁹³ These are household products that children bring into contact with their mouth and/or skin. Plasticizers in these products should be replaced similar to plasticizers in toys.⁵⁹³

13.21 INKS, VARNISHES, AND LACQUERS

13.21.1 PLASTICIZER TYPES

- dibutyl phthalate in ink for forming electronic components,⁵⁹⁸ in heat activated printing inks,⁶⁰³ and in pressure transfer ink⁶⁰⁴¹
- benzyl phthalate of high molecular weight (Santicizer 278) in phase change ink composition,^{605,616,621} in photochromic ink,⁶²⁶ in solid ink,⁶³⁰ and in reactive ink⁶³¹
- benzyl butyl phthalate in phase change ink composition,⁶¹⁰ jet ink composition,⁶²⁷ and in high electrical resistivity ink jet composition⁶³³
- dicyclohexyl phthalate (Uniplex 250) in acoustic printing ink⁶⁰⁶
- 2,2,4-methyl-1,2-pentanediol diisobutyrate (Texanol TXIB) in non-fluorescent ink,⁵⁹⁵ in fluorescent ink for writing instruments,⁶⁰⁵ and in non-rub off printing ink⁶²⁸
- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352) in pigmented solid ink⁶²³
- mineral oil in erasable ink⁵⁹⁶
- polyethylene glycol in jet ink⁶⁰²
- ethylene glycol in ballpoint pen⁶¹¹
- glycerin in jet ink⁶¹²
- polybutene in erasable ink⁵⁹⁶
- sucrose acetate isobutyrate⁵⁹⁴
- glycerol propyloxate (Arcol LHT) in solid ink⁶⁰¹
- polyester plasticizer (Uniflex 312) in piezo jet inks^{608,620}
- solid plasticizer in fusible ink jet medium⁶³²

- phosphate ester, dicarboxylic acid ester, or tricarboxylic acid ester in ink composition⁶³⁴

13.21.2 PLASTICIZER CONCENTRATION

- dibutyl phthalate: 10 wt% in heat activated printing ink,⁶⁰³ 2 to 4 wt% in pressure transfer ink,⁶⁰⁴ and 3 wt% in photochromic heliographic ink⁶³⁸
- benzyl butyl phthalate: 10 wt% in phase change ink⁶¹⁰ and up to 5 wt% in jet ink
- benzyl phthalate of high molecular weight (Santicizer 278): 9.5 wt% in reactive ink⁶³¹
- 2,2,4-methyl-1,2-pentanediol diisobutyrate (Texanol TXIB): 2 to 15 wt% in fluorescent ink for writing instruments⁶⁰⁵ and 0.5 to 3 wt% in non-rub off printing ink⁶²⁸
- sucrose acetate isobutyrate: 10 to 20 wt% in inks⁵²¹ and 18.4 wt% in lacquers for plastics⁵⁹⁴
- polyester plasticizer (Uniflex 312): 0.2 to 2 wt% in piezo jet inks^{608,620}

13.21.3 REASONS FOR PLASTICIZER USE

- solubility in solvents⁵⁹⁴
- compatibility with ink resins^{594,608,620}
- reduction of viscosity^{605,613,617}
- low viscosity of melted ink^{610,619}
- modification of rheological properties⁶¹¹
- improvement of film flexibility^{595,605,608,613,615,617,618,620,627,628,629}
- improvement of abrasion resistance⁶²⁷
- effect on rate of film formation (self-fixing)^{614,622}
- lowering minimum film formation temperature^{614,622}
- adjustment of hardness⁶⁰⁴
- lowering fusion temperature^{597,599}
- enhancement of contact between image layers⁶⁰⁰
- reduction of spherulite size^{609,624}
- preventing crystallization⁶¹⁹
- increasing crease resistance⁶²⁴
- improvement of ink adhesion^{594,603,629,630}
- improvement of gloss⁵⁹⁴
- elimination of cracking and blistering⁶¹⁵
- improvement of thermal stability⁶²³
- dilution of color concentrate⁶²³
- preventing ink from drying in cells of the gravure cylinder⁶²⁹

13.21.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- some plasticizers help to reduce spherulite size by forming small spherulitic crystalline domains. Spherulites smaller than 1 μm improve projection efficiency and increase crease resistance. These plasticizers are found to be useful: o,p-toluene sulfonamide (Uniplex 171), p-toluene sulfonamide (Uniplex 173), dicyclohexyl phthalate (Uniplex 250), dimethylisophthalate (Uniplex 270), and pentaerythritol

tetrabenzoate (Uniplex 552). The technology is especially useful in printed transparencies where projection efficiency is improved.^{609,624}

Disadvantages

- causing cracking and blistering⁶¹⁵

13.21.5 EXAMPLES OF FORMULATIONS

Metallic ink:⁵⁹⁴

Cellulose acetate propionate (CAP-482-0.5)	7.6 parts
Acrylic resin (Acryloid B-72, 100%)	3.8
Citric acid	0.05
Ethyl acetate	17.4
Sucrose acetate isobutyrate (SAIB-90)	2.6
Metallic pigment	28.0

Lacquer for plastics:⁵⁹⁴

Cellulose acetate butyrate (CAB 381-0.5)	16.6 wt%
Sucrose acetate isobutyrate (SAIB-90)	18.4
Toluene	33.4
Denaturated ethyl alcohol (Tecsol C 95%)	4.8
Ethyl acetate	13.4
Isobutyl acetate	13.4

Jet ink:⁶⁰³

Sublaprint Blue 70014	10.0 wt%
Polywax PE500	10.0
Exxon FN 3505	58.0
DisperByk 182	0.5
Vinnapas B1.5	1.5
Piccolastic A25	10.0
Polygard	5.0
Dibutyl phthalate	5.0

Jet ink with improved dye density:⁶¹²

Dye	0.9-2.6 parts
Lactic acid	0.7
Glycerin	6.0
Diethylene glycol	6.0
Surfynol 465	0.25
Proxel GXL	0.003
Filtered deionized water	84-87

Ballpoint pen ink free from leakage from its tip:⁶¹¹

Direct Black 154	7.5 wt%
Ethylene glycol	25.0
Rust-preventive lubricant	1.0
pH regulator	2.0

Antibacterial agent	0.5
Crosslinking acrylic acid polymer	0.25
Xanthan gum	0.10
Succinoglycan	0.05
Ion-exchange water	63.6

Photochromic heliographic ink:⁶³⁸

Polyvinyl resin (Rhodopas AS 85-15)	25 parts
Dibutyl phthalate	3
Epoxy plasticizer (Edenol D81)	2
Methyl ethyl ketone	35
Isopropyl acetate	32
Photochromic of class A	3

13.22 MEDICAL APPLICATIONS

13.22.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) adipate in coextruded tubing⁶⁵⁸
- dibutyl phthalate in hydrophilic coatings with hydrating agents⁶⁶⁹
- di-(2-ethylhexyl) phthalate in blood contacting applications,^{643,644} in coextruded tubing,⁶⁵⁴ in blood bags,^{666,673,674} in surface sulfonated film,⁶⁷⁵ in endotracheal tubes,⁶⁷⁷ and in radiation sterilizable medical disposables⁶⁷⁸
- diundecyl phthalate in containers for medical use⁶⁷¹
- tri-(2-ethylhexyl) trimellitate in blood contacting applications,⁶⁴⁴ in blood bags,⁶⁶⁶ and in material for flexible medical products⁶⁶⁸
- n-butyric-n-hexyl citrate in blood contacting applications⁶⁴⁴ and in medical containers⁶⁵³
- triethyl citrate in medical devices from aliphatic pocketing⁶⁷⁵
- tributyl citrate in sterilized cyanoacrylate solutions⁶⁵⁷
- acetyl tributyl citrate in sterilized cyanoacrylate solutions⁶⁵⁷
- polyethylene glycol in medical pressure-sensitive adhesive⁶⁷⁰
- glycerin in medical pressure-sensitive adhesive,⁶⁷⁰ in poly(vinyl alcohol)-based medical devices,⁶⁸⁰ and in medical devices for delivery of therapeutic agents⁶⁸²
- butyl benzosulfonamide in medical devices from aliphatic polyketone⁶⁶⁵
- polybutene in hydrocolloid adhesive⁶⁵⁹
- paraffin oil in hotmelt adhesive for disposable articles⁶⁶³
- phosphonium-based ionic liquids in biomedical grade⁶⁷⁶
- isopropyl myristate in pressure-sensitive adhesive on medical tape⁶⁸⁴
- fast leaching, temporary plasticizer in medical stents^{679,681}
- biocompatible plasticizer in drug-coated balloon⁶⁸³

13.22.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 40 wt% in blood contacting applications⁶⁴³ and 30 to 40 wt% in blood contacting applications⁶⁴⁴
- triethyl citrate: 10 wt% in medical devices from aliphatic polyketone⁶⁶⁵
- tributyl citrate: 5 to 7 wt% in sterilized cyanoacrylate solutions⁶⁵⁷

- tri-(2-ethylhexyl) trimellitate: 43 to 57 wt% in material for flexible medical products⁶⁶⁸
- paraffin oil: 15 to 25 wt% in hotmelt adhesive for disposable articles⁶⁶³

13.22.3 REASONS FOR PLASTICIZER USE

- low migration⁶⁵⁸
- none or low bleedout⁶⁶⁴
- improvement of flexibility^{567,658,671}
- reduction of hardness⁶⁶⁷
- improvement of bonding properties⁶⁵⁸
- potential use at low temperatures⁶⁷¹
- increased gas permeability⁶⁷¹
- no interference with polymerization⁶⁵⁷
- low level of moisture in cyanoacrylate applications⁶⁵⁷

13.22.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- adjustment of glass transition temperature of catheters to be between ambient and body temperature is advantageous to its performance. At ambient temperature catheter is relatively stiff to facilitate its introduction. Once temperature equilibrates with body temperature it becomes elastic.⁶⁶⁰
- plasticizer-free tubing⁶⁶⁰
- surface sulfonation retards plasticizer migration in blood products⁶⁷⁵

Disadvantages

- migration of plasticizers is a potential problem in wound dressings being in direct contact with open wounds. In pressure sensitive adhesive migration of plasticizer may also cause deterioration of properties of adhesive⁶⁵⁶
- disposal of large quantities of medical plastics presents a number of potential concerns related to plasticizers⁶⁵⁵
- debates on toxicity of di-(2-ethylhexyl) phthalate affects application of this plasticizer⁶⁵⁶
- migration of plasticizer between layers of coextruded product affects their performance⁶⁵⁸
- migration of plasticizer out of the system makes material rigid⁶⁶¹

13.22.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Materials used in biological environments must fulfil many special requirements such as they should not cause thrombosis, alterations of plasma proteins, destruction of enzymes or cellular elements of blood, adverse immune responses, or toxic, or allergic reactions.⁶⁴⁴ Materials used in medical applications are subjected to sterilization which changes their properties and introduces modifications to their surface. On the other hand, materials are intentionally modified by plasma treatment, corona discharge, etc. These modifications increase wettability and biocompatibility.⁶⁴⁴

Only a few surface layers can interact with a living system such as blood. From a study including di-(2-ethylhexyl) phthalate and tri-(2-ethylhexyl) trimellitate it was found that not so much chemical composition of plasticizer affects reactivity with blood but plasticizer's concentration on the surface and this was higher for tri-(2-ethylhexyl) trimelli-

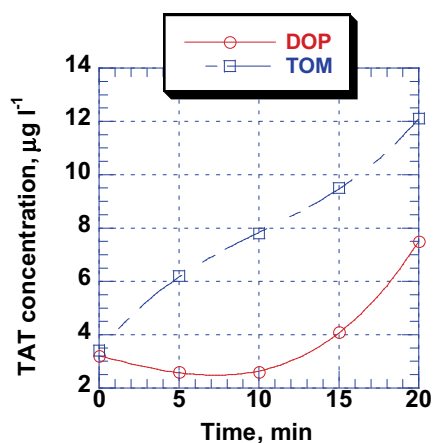


Figure 13.10. Thrombin-antithrombin III complex, TAT, concentration versus time of contact with PVC containing two plasticizers (di-(2-ethylhexyl) phthalate, DOP, and tri-(2-ethylhexyl) trimellitate, TOM). [Adapted, by permission, from Yin H Q; Zhao X B; Courtney J M; Blass C R; West R H; Lowe G D O, *J. Mater. Sci. Mater. Medicine*, **10**, No.9, Sept.1999, p.527-31.]

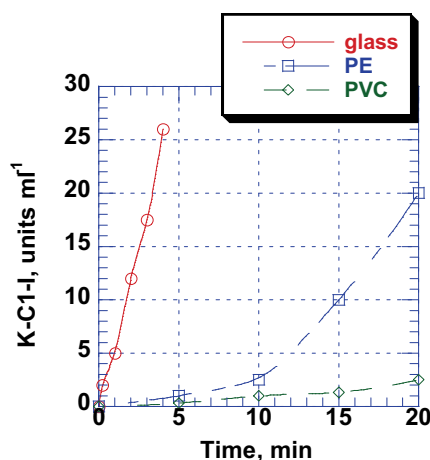


Figure 13.11. Contact activation as measured by kallikrein-C1-inhibitor concentration containing by definition 100 units per ml vs. contact time. [Data from Lindhout T; Blezer R; Maassen C; Heijnen V; Reutelingsperger C P M, *J. Mater. Sci., Mater. Medicine*, **6**, No.6, June 1995, p.367-72.]

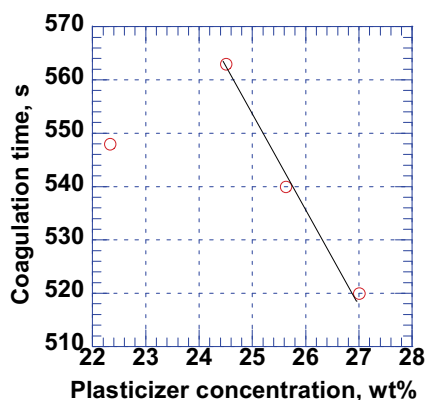


Figure 13.12. Blood coagulation time vs. di-(2-ethylhexyl) phthalate concentration in PVC materials. [Data from Kicheva Y I; Kostov V D; Chichovska M, *BioMater.*, **16**, No.7, 1995, p.575-9.]

note that glass gives still faster contact activation than polyethylene.⁶⁵¹

Figure 13.12 confirms suggestions based on studies reported in Figure 13.10. Increased amount of plasticizer in formulation causes increased concentration of plasti-

tate.⁶⁴⁴ Figure 13.10 shows the thrombin-antithrombin III complex, TAT, versus time of contact with PVC containing two plasticizers (di-(2-ethylhexyl) phthalate, DOP, and tri-(2-ethylhexyl) trimellitate, TOM). Substantially higher thrombogenicity was observed for TOM.⁶⁴⁴

In comparison with other polymeric materials such as polyethylene, polypropylene, and polyurethane, polyvinylchloride plasticized with DOP and TOM had the longest clotting time (10 min) with polyethylene having the shortest clotting time (5 min). PVC is the least thrombogenic surface and PE is the most thrombogenic surface. Figure 13.11 shows that there is very big difference in contact activation by both surfaces as measured by kallikrein-C1-inhibitor concentration. It is interesting to

cizer on the surface of test material and it reduces blood coagulation time. The presence of plasticizer on the surface makes surface less biocompatible.⁶⁵²

Some plasticizers were found to have beneficial effect on stored red blood cells.⁵⁷⁷ Lower rate of hemolysis of red blood cells was observed in the presence of di-(2-ethylhexyl) phthalate, tri-(2-ethylhexyl) trimellitate, and n-butyryltri-n-hexyl citrate. It is suggested in recent invention that even if for reasons of mechanical properties plasticizers are not needed their addition will still give benefits in this application, especially in composition with vitamin E used as antioxidant.⁶⁵³

Surface of plasticized materials is modified by various means such as surface irradiation, crosslinking, or grafting to reduce transfer of plasticizer to the surface as well as increase its biocompatibility.

Figure 10.59 shows that addition of plasticizer hinders degradation of color of plasticized PVC during γ -sterilization.⁶⁵⁰ This is explained by dilution which decreases probability of formation of polymer excited states but perhaps also helps to transport HCl more effectively to stabilizer by which its autocatalytic effect is reduced.

13.22.6 EXAMPLES OF FORMULATIONS

Composition of medical containers:⁶⁵³

PVC	59 parts
Vitamin E	18
n-butyryltri-n-hexyl citrate	15
Tri-(2-ethylhexyl) trimellitate	9
Epoxidized soybean oil	3
Cadmium-zinc stabilizer (CZ-11)	0.1
Ethylene bis-stearamide wax (Acrawax)	0.1

Material for flexible medical products:⁶⁶⁶

PVC resin (UHMW)	100 parts
Tri-(2-ethylhexyl) trimellitate	120
Epoxidized soybean oil	5
Calcium-zinc stabilizer	0.32
Mineral oil	0.2

13.23 MEMBRANES

13.23.1 PLASTICIZER TYPES

- di-(2ethylhexyl) sebacate in ion-exchange membrane,⁶⁸⁵ in ion-selective membrane,⁵⁹⁸ and in polycation detection membrane⁷⁰³
- diisobutyl phthalate in sensor membrane⁷⁰⁴
- benzyl butyl phthalate in polyurethane membrane^{697,700,705} and in masonry membrane⁷⁰⁹
- diethylene glycol dibenzoate in polyimide membranes⁶⁸⁸
- polyethylene glycol in osmotic membrane⁶⁹⁴
- glycerin in PVC sensor⁷⁰²
- 2-nitrophenyl octyl ether in ion-selective membrane^{686,690,693}
- liquid paraffin in multilayer porous membrane^{710,711}

- aliphatic polyesters of dibasic acids⁷¹²
- petroleum-based oil in waterproofing membrane⁷¹³

13.23.2 PLASTICIZER CONCENTRATION

- benzyl butyl phthalate: up to 5 wt% in polyurethane membrane⁶⁹⁷

13.23.3 REASONS FOR PLASTICIZER USE

- lowering glass transition temperature^{686,687,688}
- glass transition below room temperature allows to use material as ion-selective membrane⁶⁸⁸
- lowering viscosity of melt during processing⁶⁹⁶
- increase in flexibility^{697,700,705}
- increase of membrane durability^{697,700,705}
- increase in elongation⁶⁸⁷
- improved toughness⁶⁸⁷
- improvement of sound insulation⁷⁰⁶
- improvement of electric conductivity⁷⁰⁷

13.23.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- microporous membranes can be obtained by extracting plasticizer from previously formed thin sheet⁶⁹⁹
- plasticizers having solubility parameters between 7.3 and 8.4 (e.g., petroleum, lubricating, fuel, linseed and tall oils), are useful in production of microporous polyolefin membranes⁶⁹⁹

Disadvantages

- diethylene glycol dibenzoate decreases decomposition temperature of polyimide⁶⁸⁸

13.24 MICROSPHERES

13.24.1 PLASTICIZER TYPES

- triethyl citrate in ethylcellulose microspheres⁷¹⁴
- acetyl triethyl citrate in coating of swellable hydrogel microspheres⁷¹⁶

13.24.2 PLASTICIZER CONCENTRATION

- triethyl citrate: 10-30 wt% in ethylcellulose microspheres⁷¹⁴

13.24.3 REASONS FOR PLASTICIZER USE

- decrease of glass transition temperature^{714,715}
- increase of diffusion rate of drugs⁷¹⁵
- changes in surface morphology and pore volume can be made by regulating concentration of plasticizer⁷¹⁴

13.25 PAINTS AND COATINGS

This section only includes plasticizers which are used in paints and coatings used in civil engineering applications. Formation of permeable films, such as in controlled release applications is fully discussed in Section 13.26 devoted to pharmaceutical products.

13.25.1 PLASTICIZER TYPES

- dibutyl phthalate⁷¹⁹ in corrosion-inhibiting coating,⁷²⁸ in floor finishes,⁷⁴⁴ in chip-resistant automotive coatings,⁷⁴⁵ in sulfonated alkyd waterborne coating,⁷⁵² in temporary protective coating,⁷⁵³ in cellulose based coating,⁷⁵⁷ in photocurable road markings,⁷⁵⁹ and in clear coating⁷⁶⁹
- benzyl butyl phthalate in roof coatings,⁷³¹ in waterborne acrylic paints,⁷⁴⁸ in corrosion preventive coatings⁷⁸³
- alkyl benzyl phthalate (Santicizer 278) in sound damping coating⁷⁵⁰ and in vinylidene fluoride powder coatings⁷⁶⁶
- di-(2-ethylhexyl) phthalate,^{719,732} in chip-resistant automotive coatings,⁷⁴⁵ in photocurable road markings,⁷⁵⁹ in animal resistant coatings,⁷⁶⁸ in radiation cured coating,⁷⁷⁴ and in coating to protect outdoor fixtures⁷⁷⁵
- C₇ to C₁₁ phthalate (Palatinol 711) in chip-resistant, vibration-damping, automotive coatings⁷⁶³
- diisononyl phthalate in chip-resistant automotive coatings⁷⁴⁵
- diisodecyl phthalate in self-levelling composition for automotive industry⁷³⁵
- di-(2-ethylhexyl) adipate in surface covering⁷⁷⁹
- diethylene/dipropylene glycol dibenzoate (Benzoflex 50) in protective coating for tire sidewalls⁷³³
- neopentyl glycol dibenzoate (Uniplex 512) in water-based coating⁷⁴⁹
- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352) in antiblock coating for hotmelt adhesives,⁷⁴² in powder coatings,⁷⁷⁷ and in powder coatings for wood⁷⁸⁰
- citric acid ester plasticizer in moisture resistant biodegradable coating⁷⁸⁵
- toluene-o,p-ethylsulfonamide in laser markable coatings,⁷²⁶ in corrosion prevention,⁷³⁴ and in cathodic corrosion prevention⁷⁵⁴
- N-butylbenzene sulfonamide (Uniplex 214) in polyamide-based powder coating⁷⁶⁵
- di-(2-phenoxyethyl) formal (Desavin) in polyurethane anticorrosive coatings⁷⁶²
- chloroparaffins⁷²³ in antifouling paint composition^{730,761} and in coating which prevents marine organism attachment⁷⁸¹
- diethylene glycol butyl ether in curable coating containing exfoliated silicate⁷³⁷
- tributoxylethyl phosphate in floor finish composition^{744,771}
- tricresyl phosphate in coating which prevents marine organism attachment⁷⁸¹
- polybutene (e.g., Indopol 14) in thermoplastic coating⁷⁶⁴
- polyethylene glycol in abrasive article⁷⁵¹ and in shellac enteric coatings⁷⁸⁶
- polypropylene glycol alkylphenyl ether in metal coatings⁷³⁶
- propylene glycol in temporary masking coatings⁷²⁹
- glycerin in slip control coating based on silicone,⁷⁴⁰ in biocidal coating composition,^{755,767} and in protective coating for tire sidewalls⁷⁷⁰
- toluene-o,p-ethylsulfonamide (Uniplex 108) in laser markable coatings⁷²⁶ and in cathodic corrosion prevention system^{734,754}
- coconut oil alkyd resin in traffic marking paint⁷¹⁸
- acrylic polymeric plasticizer (Carboset 515) in composition which protects paint from scratching⁷³⁹

- atactic polypropylene (molecular weight 5,000 to 10,000 daltons) in coating of filler for highly filled materials (up to 80 wt% filler)⁷⁴³
- soya lecithin in moisture barrier coating⁷⁷⁶

13.25.2 PLASTICIZER CONCENTRATION

- dibutyl phthalate: 1.35 wt% in temporary protective coating⁷⁵³ and 1 wt% in clear coating⁷⁶⁹
- benzyl butyl phthalate: up to 5 wt% in roof coatings⁷³¹ and 1.5-3 wt% in anticorrosive coatings⁷⁸³
- alkyl benzyl phthalate (Santicizer 278): up to 10 wt% in sound damping coating⁷⁵⁰
- di-(2-ethylhexyl) phthalate: 5 wt% in animal-resistant coatings⁷⁶⁸
- C₇ to C₁₁ phthalate (Palatinol 711): 3 to 10 wt% in chip-resistant, vibration-damping, automotive coatings⁷⁶³
- diisodecyl phthalate: 25 to 35 wt% in self-levelling composition for automotive industry⁷³⁵
- diethylene/dipropylene glycol dibenzoate (Benzoflex 50): 1 to 3 wt% in protective coating for tire sidewalls⁷³³
- 1,4-cyclohexane dimethanol dibenzoate (Benzoflex 352): 0.9 to 1.3 wt% in anti-block coating for hotmelt adhesives⁷⁴² and 2 to 12 wt% in powder coatings⁷⁷⁷
- neopentyl glycol dibenzoate (Uniplex 512): 2 to 5 wt% in water-based coating⁷⁴⁹
- toluene-o,p-ethylsulfonamide: up to 3 wt% in laser markable coatings,⁷²⁶ 2.5 to 5 wt% in corrosion prevention,⁷³⁴ and 5 wt% in cathodic corrosion prevention⁷⁴⁴
- di-(2-phenoxyethyl) formal (Desavin): 1 to 3 wt% in polyurethane anticorrosive coatings⁷⁶²
- tributoxylethyl phosphate: 1 to 3.5 wt% in floor finish composition⁷⁷¹
- polybutene (e.g., Indopol 14): 1 to 6 wt% in thermoplastic coating⁷⁶⁴
- acrylic polymeric plasticizer (Carboset 515): 3.75 wt% in composition which protects paint from scratching⁷³⁹

13.25.3 REASONS FOR PLASTICIZER USE

- decrease in glass transition temperature^{719,720,744}
- change of rheological properties^{744,750,779}
- promotion of flow⁷²⁸
- reduces plastisol viscosity⁷⁸⁴
- improvement in film-forming properties⁷⁴⁴
- imparts plasticity⁷⁴⁵
- increase of flexibility^{719,723,727,756}
- improvement of formability⁷²⁷
- decrease of film rigidity and stiffness⁷²³
- increase of elongation^{719,720}
- improvement of mechanical strength⁷²⁷
- improvement of impact resistance⁷¹⁹
- reduces peeling⁷³⁹
- reduces chipping⁷³⁹
- affects wettability⁷²³

- increases adhesion^{719,723,739}
- influence permeability of water and gases⁷²³
- decreases tendency of film to crack^{723,739}
- enhances coating coalescence⁷⁴⁰
- decreases melt flow temperature^{777,780,782}

13.25.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- close match of solubility parameters of plasticizer and polymer implies high efficiency of plasticizer.⁷²⁰ Such plasticizers reduce glass transition the most effectively and are not likely to bloom out of coating
- tributoxylethyl phosphate works together with coalescing agent to accelerate conversion⁷⁴⁴
- plasticizer does not change water content of hydrogel materials but changes their swell factor⁷⁶⁰
- soya lecithin acts as humectant and attracts moisture which plasticizes material. In this invention⁷⁷⁶ it was found that in spite of attracting some moisture, lecithin did not compromise moisture barrier properties of coatings⁷⁷⁶

Disadvantages

- plasticizer increases erodibility of abrasive composite and softens binder^{758,773}
- plasticizer may migrate to surface, degrade due to UV exposure and initiate degradation of polymer (unlikely mechanism)⁶⁸⁰

13.25.5 EXAMPLES OF FORMULATIONS

Temporary, protective coating:⁷⁵³

Prepolymer (Neorad NR-3709)	49.52 wt%
Release agent (lecithin)	0.5
Photoinitiator (triphenyl phosphine oxide)	0.4
Water	46.71
Dibutyl phthalate	1.35
Thickener (DSX-1550)	0.84
Leveling agent (BYK-346)	0.13
Antifoam agents (BYK-022 and 024)	0.4
Blue dye	0.15

Cathodic corrosion prevention system:⁷⁵⁴

Urethane resin	51.0 wt%
Phenolic resin	5.0
Polyaniline powder (Versicon)	7.0
Aluminum powder (Al-120)	12.0
Ethyl toluenesulfonamide (Uniplex 108)	5.0
VM&P naphtha	3.0
Xylene	3.0
Mineral spirits	14.0

Animal-resistant coating:⁷⁶⁸

10% Tungsten carbide whiskers	10 wt%
Guar gum	20
Diocetyl phthalate	5
Methyl methacrylate	65

Clear coatings:⁷⁶⁹

Acrylic latex	150 parts
Deionized water	36
Dowanol PnB (coalescent)	14.4
Dibutyl phthalate (plasticizer)	2.2
Acrysol QR-708 (thickener)	1.0

13.26 PHARMACEUTICAL PRODUCTS**13.26.1 PLASTICIZER TYPES**

- glycerin in push-fit capsules,^{799,800,802,803,805,806} in sustained release composition,⁸²⁵ in bright white coating,⁸³⁸ in chewable adsorbates,⁸⁴⁶ in hydroxypropyl methylcellulose tablet coating,⁸⁵⁴ and in skin-bioadhesive patches⁸⁵⁵
- sorbitol in push-fit capsules^{799,800,802,803,805,806} and as antiplasticizer in polymeric drug delivery system⁸⁵⁶
- soya lecithin in moisture barrier coating of tablets⁸⁰¹
- polyethylene glycol⁸³¹ in tablet formation,⁸⁰⁸ in edible coating,⁸¹⁷ in odor-masking coating,⁸²⁰ in sustained release composition,⁸²⁵ in bright white coating,⁸³⁸ in enteric film coating,⁸⁴⁵ in time release tablet,⁸⁴⁷ in Eudragit S100 matrix pellets,⁸⁵¹ in hydroxypropyl methylcellulose tablet coating,⁸⁵⁴ in skin bioadhesive patches,⁸⁵⁵ and in pharmaceutical composition⁸⁶¹
- propylene glycol in composition for oral bioavailability,⁸¹¹ in composition for lipid lowering,⁸²⁹ and in oral composition⁸³⁶
- triethyl citrate in plasticization of acrylic resins (Eudragit) in controlled release applications,^{789,792} in plasticization of ethyl cellulose,^{790,791} in controlled release coating based on ethyl cellulose,⁸⁰⁸ in production of solid dosage forms,⁸¹⁹ in anti-ulcer drug coating,⁸²⁴ in sustained release coating,⁸²⁶ in laminar time release,⁸³⁴ in enteric dosage forms,⁸⁴² in enteric film coating,⁸⁴⁵ in chewable adsorbates,⁸⁴⁶ and in control release preparation containing morphine⁸⁴⁸
- glycerol tributyrate in plasticization of ethyl cellulose^{790,791}
- diethyl tartrate in plasticization of ethyl cellulose^{790,791}
- triacetin in plasticization of ethyl cellulose,⁷⁹² in edible coating containing propylene glycol alginate,⁷⁹⁶ in controlled release coating based on ethyl cellulose,⁸⁰⁸ in coating of vitamin tablets,⁸⁰⁹ in dosage form for administration of hydrophilic drugs,⁸¹² in plasticization of hydroxypropylmethyl cellulose,⁸²³ in controlled release tablet,⁸³⁵ in melt extruded systems,⁸⁴⁹ and in Eudragit-S and Eudragit-L tablets⁸⁵²
- triethyl citrate in microspheres, Eudragit S100 matrix pellets,⁸⁵¹ and in enteric Eudragit L30D-55 coated pellets⁸⁵³
- acetyl tributyl citrate⁸⁵⁰ in xenobiotic receptor

- diethyl phthalate in plasticization of hydroxypropylmethylcellulose for glucose uptake enhancers,⁷⁰⁷ in controlled release coating based on ethyl cellulose,⁸⁰⁸ in controlled release capsule,⁸¹⁰ in enteric coating,⁸³⁰ in cholesterol lowering drug,⁸⁴¹ in enteric dosage forms,⁸⁴² and in sustained release formulation⁸⁴⁴
- dibutyl phthalate in plasticization of methylmethacrylate copolymer (Eudragit RSPN)⁸¹⁵ and in antacid composition⁸⁴⁰
- dibutyl sebacate in controlled release coating based on ethyl cellulose⁸⁰⁸
- diethyl sebacate in antacid composition⁸⁴⁰
- oleyl oleate in transdermal delivery device⁸²⁸
- D- α -tocopheryl PEG 1000 succinate⁸⁴⁹ in melt extruded systems
- ibuprofen, chlorpheniramine maleate, and metoprolol tartrate acted as plasticizers of Eudragit RS⁸⁵⁷
- carbon dioxide in hot melt extrusion process of pharmaceutical polymers⁸⁵⁸
- solid plasticizer in direct coating of solid dosage forms⁸⁵⁹
- hygroscopic plasticizer⁸⁶⁰ in stable pharmaceutical composition

13.26.2 PLASTICIZER CONCENTRATION

- glycerin: 3.5 to 7.5 wt% in sustained release composition^{825,843} and 10 wt% in skin-bioadhesive patches⁸⁵⁵
- soya lecithin: 1 to 6 wt% in moisture barrier coating⁸⁰¹
- triethyl citrate: 12.5 phr (10.7 wt% of dry contents) in plasticization of acrylic resins (Eudragit),⁷⁸⁹ 11 wt% in production of solid dosage forms,⁸¹⁹ and 10 wt% in control release preparation containing morphine⁸⁴⁸
- acetyl tributyl citrate for pulsatile delivery of antiarrhythmic agent⁷⁹⁸
- triacetin: 20 to 25 wt% in edible coating containing propylene glycol alginate,⁷⁹⁶ 20 phr in dosage form for administration of hydrophilic drugs,⁸¹² 2 to 15 wt% in controlled release tablet⁸³⁵
- polyethylene glycol: 31 to 35 wt% of dry composition in edible coating⁸¹⁷ and 7.5 to 10 in dextrin-based film coating⁸⁴³
- propylene glycol: 7.5 wt% in composition for oral bioavailability⁸¹¹ and 7.5 to 10 wt% in sustained release composition⁸²⁵
- diethyl phthalate: 0.1 wt% in controlled release capsule,⁸¹⁰ 12.5 wt% in enteric coating,⁸³⁰ and 10 to 15 wt% in cholesterol lowering drug,⁸⁴¹ and 15 phr in acrylic coating (Eudragit RS30D)⁸⁴⁴

13.26.3 REASONS FOR PLASTICIZER USE

- to regulate release rate of therapeutic compound^{804,815}
- to decrease of glass transition temperature^{797,804,814,819}
- to decrease temperature of coalescence⁷⁹⁷
- improvement of coating flexibility^{801,820} that it can stretch without breaking^{797,820}
- to prevent film cracking⁸⁴²
- improvement of film-forming properties⁸³²
- improvement of film appearance⁸²⁰
- to obtain desirable mechanical properties⁸¹⁸

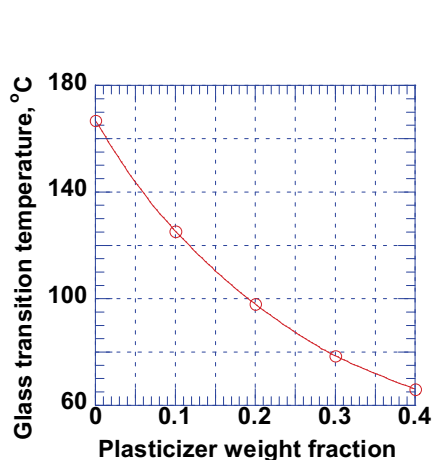


Figure 13.13. Glass transition temperature of ethyl cellulose vs. weight fraction of tributyl citrate. [Data from Beck M I; Tomka I, *J. Polym. Sci.: Polym. Phys. Ed.*, 35, No.4, March 1997, p.639-53.]

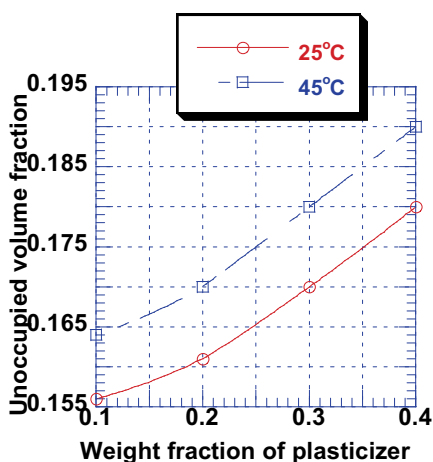


Figure 13.14. Unoccupied volume fraction in ethyl cellulose vs. weight fraction of tributyl citrate. [Data from Beck M I; Tomka I, *J. Polym. Sci.: Polym. Phys. Ed.*, 35, No.4, March 1997, p.639-53.]

13.26.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- soya lecithin acts as humectant and attracts moisture which plasticizes material. In this invention⁸⁰¹ it was found that in spite of attracting some moisture, lecithin did not compromise moisture barrier properties of coating
- plasticizers such as glycerin, sorbitol, and polyethylene glycol alter release rate of therapeutic compounds (see more on this subject in Section 13.21.5).⁸⁰⁴ The regulation of release rate can be done by selection of plasticizer type and its concentration⁸⁰⁴
- formation of acid resistant protective coating which disintegrates at pH=4⁸³⁹

Disadvantages

- a chemotherapy drug paclitaxel is very hydrophobic and must be dissolved in a mixture of ethyl alcohol and surfactant.⁷⁹⁴ Because of presence of alcohol (especially concentrated in undiluted form) it is likely to extract and transfer to body di-(2-ethylhexyl) phthalate used in production of tubes and bags used for delivery of fluids to patients. Several options are used for storage of these and other preparations (atherosclerosis)⁷⁹⁵ drugs. These include glass, polyolefin, polypropylene⁷⁹⁵ or PVC plasticized with tri-(2-ethylhexyl) mellitate.⁷⁹⁴
- inclusion of plasticizers generally makes coatings more tacky (some combinations of coatings show that plasticizer may also act as mild detackifier⁸¹⁴)
- migration of plasticizer affects shelf life of drug⁸¹⁶
- bleeding of excessive plasticizer⁸³⁷
- excessive amounts of plasticizer cause that tablets stick to each other⁸³⁹

13.26.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

In some applications very low processing temperature is necessary. For example, temperature sensitive additives cannot be introduced into implants because they will degrade dur-

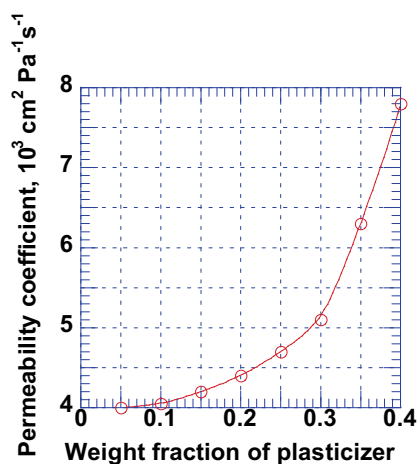


Figure 13.15. Oxygen permeability coefficient of ethyl cellulose vs. weight fraction of tributyl citrate. [Data from Beck M I; Tomka I, *J. Polym. Sci.: Polym. Phys. Ed.*, 35, No.4, March 1997, p.639-53.]

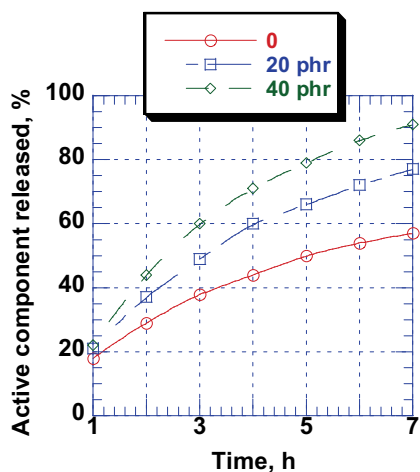


Figure 13.16. Percentage of Na Diclofenac released from controlled release tablet vs. time for different concentrations of dibutyl phthalate used to plasticize methylmethacrylate copolymer (Eudragit RSPN). [Data from Mulye N, **US Patent** 6,437,000.]

ing implant shaping. For these cases, a new processes of plasticization was developed. The process is known as Controlled Expansion of Saturated Polymers, CESP.⁷⁸⁸ Carbon dioxide is absorbed into polymer at high pressure and low temperature. Plasticization action of carbon dioxide makes polymer formable at temperatures as low as 25-35°C because its glass transition is very low at this saturated state. Polymer expands in mold cavity and finally gas is extracted and polymer gradually returns to normal glass transition temperature.

Figure 13.13 shows that glass transition temperature of ethyl cellulose decreases along with increasing fraction of tributyl citrate. Figure 13.14 shows that the unoccupied volume fraction increases with addition of plasticizer as it does with increase in temperature. Figure 13.15 shows that permeability of gas increases when more plasticizer is added. Figure 13.16 shows that concentration of plasticizer determines the rate of active substance released from pharmaceutical tablets designed for controlled release. This set of data shows the reasons for use of plasticizers in pharmaceutical industry.

13.26.6 EXAMPLES OF FORMULATIONS

Coating of vitamin tablets by spraying process:⁸⁰⁹

Polydextrose	68.38 wt%
Kelgin LV	4.18
Alcolec F-100	2.51
Triacetin	2.09
PEG 8000	6.27
R-40 lake	12.50
TiO ₂	4.00

Controlled release capsule composition:⁷¹¹

Active ingredient	250 mg/capsule
Microcrystalline cellulose	125
Lactose BP	125
Cellulose acetate phthalate	50
Diethyl phthalate	5

Film coating in which plasticizers acts as mild detackifiers:⁸¹⁴

Polyvinyl alcohol	47.65 wt%
Talc	19.67
Soya lecithin	6.33
Glycerin	5.35
TiO ₂	2.31
FD&C Red 40 Lake	15.08
FD&C Yellow 6 Lake	3.41
FD&C Blue 2 Lake	0.20

Enteric coating:⁸³⁰

Eudragit L-30-D	6.892 parts
Diethyl phthalate (pH adjusted to 5.0)	1.039

13.27 PHOTOGRAPHIC MATERIALS**13.27.1 PLASTICIZER TYPES**

- tributyl citrate in blue sensitive layer⁸⁶²
- dibutyl sebacate in red sensitive layer⁸⁶²
- triphenyl phosphate in plasticization of triacetyl cellulose^{866,867}
- phosphoric acid plasticizer in cellulose ester, polarizing film, and liquid crystal display⁸⁷⁶
- dicyclohexyl phthalate in transfer material for sepia images⁸⁷⁰
- dibutyl phthalate in base film⁸⁷¹ and in polymer overcoat⁸⁷²
- di-(2-ethylhexyl) phthalate in base film⁸⁷¹ and in molded articles for photosensitive material⁸⁷³

13.27.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 0.1 to 5 wt% in molded articles for photosensitive material⁸⁷³

13.27.3 REASONS FOR PLASTICIZER USE

- to control glass transition temperature⁸⁶⁹
- to provide film flexibility^{863,875,877}
- as film-forming aid⁸⁶⁴
- to enhance dispersion of phosphor⁸⁶⁵
- to aid fusing step⁸⁶⁶
- to lower melt viscosity⁸⁶⁸

13.28 PIPES

13.28.1 PLASTICIZER TYPES

- dibutyl phthalate in polyvinylbutyral conductive pipe⁸⁷⁹
- triethyl citrate in methacrylate copolymers⁸⁸⁷
- ethylene-vinyl acetate-carbon monoxide copolymer (Elvaloy 742) in pipe liner composition⁸⁸⁹
- N-butyl benzene sulfonamide in polyamide-11⁷⁶⁶ and in polyamide-12⁸⁸⁶
- sulfonamide plasticizer in hollow structure for conveying refrigerant fluids⁸⁹⁰
- alkaline salt of sulfonated melamine (Sikament 86) as a superplasticizer of cementitious pipe⁸⁸⁵

13.28.2 PLASTICIZER CONCENTRATION

- N-butyl benzene sulfonamide: 15 phr in polyamide-12⁸⁸⁶
- ethylene-vinyl acetate-carbon monoxide copolymer (Elvaloy 742): 26 phr in PVC pipe liner⁸⁸⁹

13.28.3 REASONS FOR PLASTICIZER USE

- lowering of glass transition temperature^{887,889}
- low volatility⁸⁸⁷
- low migration⁸⁸⁰
- stability to discoloration under long-term heat aging^{887,888}
- stability to long-term exposure to radiation above 380 nm⁸⁸⁸

13.28.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- ethylene-vinyl acetate-carbon monoxide copolymer is permanent plasticizer of PVC⁸⁸⁹

Disadvantages

- polyamide-11 based pipes must be plasticized to obtain required mechanical performance but pipes containing some plasticizers are not resistant to gasoline⁸⁸⁰
- physical loss of plasticizer ultimately leads to unplasticized thermoplastic which is unable to withstand mechanical load^{881,882}
- high volatility of plasticizer causes bubble formation during processing⁸⁸⁷

13.28.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Burst pressure is the most important measurable parameter of pipe. Its measurement allows for calculation of hoop stress, σ , which characterizes strength of pipe. The hoop stress is calculated from the following equation:

$$\sigma = \frac{D_o}{2e_o} p_m \quad [13.2]$$

where:

- D_o arithmetic average between internal and external diameter
- e_o pipe thickness
- p_m maximum recorded pressure in burst test.

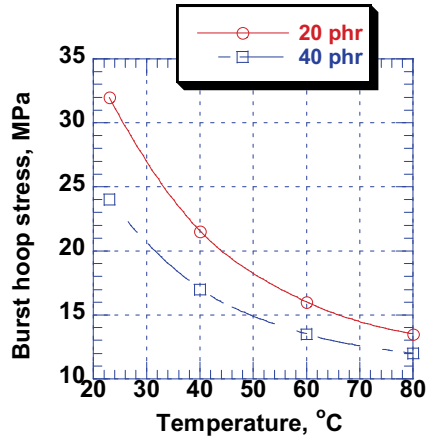


Figure 13.17. Burst hoop pressure versus temperature for polyamide12 pipe plasticized with 20 and 40 phr of plasticizer. [Data from Germain Y, *Polym. Eng. Sci.*, **38**, No.4, April 1998, p.657-61.]

Figure 13.17 that both temperature increase and plasticizer concentration increase reduce burst hoop pressure.

In order to maximize pipe performance, the plasticization is not frequently used unless required by a brittle nature of polymer (e.g., polyamide). Formulations in the next section show that the most popular pipes are used without plasticizer.

13.28.6 EXAMPLES OF FORMULATIONS

Basic formulation of rigid PVC pipe:

Suspension PVC	100 parts
Impact modifier	5
Processing aid	1
Calcium carbonate	20-30
Thermal stabilizer (lead now replaced by CaZnMg)	4

Pipe liner composition:⁸⁸⁹

PVC (Formolon 622)	100 parts
Stabilizer (Advastab TM 694)	1.313
Internal lubricant (calcium stearate)	0.413
External lubricant (Wax 355 Hoechst Celanese)	1.25
Process aid (Paraloid K-175)	1.00
Process aid (Paraloid K-120 N)	2.78
Plasticizer (Elvaloy 742P)	26.00
UV stabilizer (titanium dioxide)	0.5

13.29 ROOFING MATERIALS

13.29.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) adipate in coal tar membrane containing nitrile rubber,^{895,896} in membrane based on polyurethane reinforced asphalt,⁹⁰⁸ and in roofing adhesive⁹²¹
- di-(2-ethylhexyl) phthalate in SEBS modified asphalt mixture⁹⁰⁰
- benzyl butyl phthalate in low slope roofing system containing polyurethane⁸⁹⁹

- hexyl decyl phthalate in membrane based on chlorosulfonated polyethylene⁹¹⁶ and in polyvinylchloride⁹¹⁹
- C₁₁ phthalate (Palatinol 11P-E) in polyvinylchloride membrane⁹²¹
- tri-(2-ethylhexyl) phosphate in chlorosulfonated polyethylene and chlorinated polyethylene blend⁹⁰⁵
- tri-(2-ethylhexyl) trimellitate in chlorinated polyethylene mastic composition⁹¹⁰ and in polybutadiene roofing membrane⁹¹¹
- tricresyl phosphate in flame-retarded polyurethane composition⁹¹⁴
- naphthenic oil in SEBS modified asphalt mixture,⁹⁰⁰ in skid-resistant roofing underlayment,⁹⁰² coal tar pitch formulation,⁹⁰⁷ and in ethylene copolymer composition⁹¹³
- aromatic oil (e.g., Sundex 790T) in bitumen-based waterproofing membrane⁹¹⁸
- polyisobutylene in adhesive tape for roofing membranes,⁸⁹³ in sealing tape for rubber membranes,^{898,901,903} in asphalt based liquid membrane,⁸⁹⁹ and in cured elastomeric roofing composition based on EPDM⁹⁰⁴
- atactic polypropylene in bituminous composition⁹¹⁷
- ethylene-vinyl acetate-carbon monoxide copolymer (Elvaloy 742) in polyvinylchloride membrane⁹²⁰

13.29.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) adipate: 10 wt% in coal tar membrane containing nitrile rubber^{895,896}
- tricresyl phosphate: 8 to 15 wt% in flame-retarded polyurethane composition⁹¹⁴
- naphthenic oil: 2 to 10 wt% in ethylene copolymer composition⁹¹³
- polyisobutylene: 5 to 9 wt% in adhesive tape for roofing membranes,⁷⁷⁸ 35 to 55 phr in sealing tape for rubber membranes,^{898,901} and 40 to 50 phr in roofing tape⁹⁰³

13.29.3 REASONS FOR PLASTICIZER USE

- reduces glass transition temperature⁸⁹⁹
- improves low temperature properties of product⁹⁰⁸
- lowers viscosity^{899,907,909}
- compatibilizes rubber and asphalt^{900,909,911,918}
- helps to obtain surface tack in adhesive tapes^{898,903}
- aids dispersion of other components⁹⁰⁸
- improves production of polyurethane prepolymers⁹⁰⁸
- reduces amount of tackifier required⁹⁰¹

13.29.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Disadvantages

- loss of plasticizer results in a loss of flexibility, embrittlement, and decreased cold crack resistance⁹¹¹
- paraffinic oils bleed from ethylene copolymer compositions⁹¹³

13.29.5 EXAMPLES OF FORMULATIONS

Single-ply roofing membrane based on chlorosulfonated polyethylene and chlorinated polyethylene blend:⁹⁰⁵

Chlorosulfonated polyethylene (Hypalon 45)	51 parts
Chlorinated polyethylene (Tyrin 725)	49
Ultralow density polyethylene (Attane 4404)	20
Magnesium hydroxide (Versamag tech)	5
Stearamide (Kemamide S)	0.50
Fatty acid ester (Struktol WB 222)	2.50
Modified barium metaborate (Busan 11-MI)	15
Calcium carbonate (Camel-wite)	62
Calcined kaolin (Icecap K)	20
TiO ₂	20
EPDM	6
Cycloaliphatic epoxide (ERL 4221)	2.20
Stabilizer (Mark 1117)	1
Aluminum trihydroxide (Micral 932)	20
#2175 Blue MB	0.002
Polyethylene glycol (Carbowax 3350)	1
Tri-(2-ethylhexyl) phosphate	6
Antioxidant (Irganox 1010)	1
Thioester stabilizer (Carstab DLTPD)	2

Chlorosulfonated polyethylene based membrane:⁹¹⁶

Chlorosulfonated polyethylene (Hypalon 45)	50.0 parts
Polyvinylchloride	2.5
Hexyl decyl phthalate	10
Ba-Cd-Zn thermal stabilizer	2
Biocide (Vinyzene BP-5)	2
Polymethylmethacrylate	2
MgO	2.5
Epoxy resin (Epon 828)	3
Antioxidant (Irganox 1076)	0.7
Polyethylene glycol	1
Kenamid 5	0.4
CaCO ₃	50
TiO ₂	15

Coal tar pitch based membrane:⁹⁰⁷

Coal tar pitch	59.5 wt%
Naphthenic oil (Tufflo 4070)	15.0
SBS block polymer (T-6302)	15.0
Polybutadiene (B-225)	0.5
CaCO ₃	10.0

Roofing sealant for EPDM membranes:⁸⁹⁷

EPDM (Trilene 77)	70 parts
Styrene-ethylene/propylene (Kraton G-1701)	50
Polyisobutylene (Vistanex CP-24)	80
Polyethylene wax	30
Antioxidant	2
Carbon black	20
Treated calcium carbonate	750
Metallic oxide silica	20
Tackifier(s)	95
Lime	20
Oleic acid	2
Organoclay	40
Mineral oil (Drakeol 10B)	40
Naphtha	100
VM&P naphtha	200

13.30 TIRES**13.30.1 PLASTICIZER TYPES**

- texanol isobutyrate in deflation-proof pneumatic tire⁹³⁴
- mixture of glycol dibenzoates (Benzoflex 9-88-SG) in industrial solid tires⁹⁴¹
- aromatic oil in tread of pneumatic tire,^{927,929} in tire treads,^{930,932,933,936} and in tire having increased tread life⁹⁴⁰
- naphthenic oil in pneumatic tire^{926,929} and in carcass⁹³⁷
- paraffinic oil (e.g., Flexon 876) in isobutylene elastomer,⁹²⁸ in pneumatic tire,⁹²⁹ and in innerliner⁹⁴¹
- heavy oil fraction free from polycyclic aromatics in rubber mixture⁹⁴³
- mineral oil in rubber mixture with low heat build-up⁹⁴⁴ and in tire treads⁹⁴⁷
- triethylene glycol caprylate in tread composition⁹²³
- fatty acid ester in polyurethane tire fillings⁹⁴⁵
- butylbenzenesulfoamide in polyamide innerliner of a pneumatic tire⁹⁴⁶

13.30.2 PLASTICIZER CONCENTRATION

- aromatic oil: 15 wt% in tire treads,^{930,932} 8 wt% in tire treads,⁹³³ and 6 wt% in tire having increase tread life⁹⁴⁰
- paraffinic oil (e.g., Flexon 876): 10 wt% isobutylene elastomer⁹²⁸ and 5 to 20 wt% in innerliner⁹⁴²

13.30.3 REASONS FOR PLASTICIZER USE

- reduces elastic and complex moduli⁹³¹
- improves between layer adhesion⁹²³
- compatibilizer of starch and rubber⁹²⁴
- modified starch/plasticizer composite improves tear resistance⁹²⁴
- physical/chemical interaction with polymer or other additives⁹²⁴

13.30.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- low temperature plasticizers in tire tread increase ice traction⁹³⁸

Disadvantages

- plasticizers in tread decrease abrasion resistance⁹³⁹

13.30.5 EXAMPLES OF FORMULATIONS

Tire tread compound reinforced with silica:⁹²⁵

E-SBR (Krynox 1721)	103 parts
S-SBR (Buna VSL 5025-1)	103
Butyl rubber (Buna CB 25)	25
Silica (Vulkasil S)	70
Filler activator (Si 69 reinforcing additive)	6
Carbon black (N234)	6
Aromatic mineral oil (Renopal 450)	8
Antiozonant (Vulkanox 4020)	1.5
Antioxidant (Vulkanox HS/LG)	1.5
Zinc oxide	3
Stearic acid	2
Accelerator (Vulkacit CZ/C)	1.8
Accelerator (Vulkacit D/C)	2
Sulfur	1.5

Tread compound:⁹³²

Styrene-butadiene rubber (Buna VSL 5025-0)	100 parts
Antioxidant (Vulkanox BKF)	0.5
Aromatic oil (Renopal 4500)	37.5
Hydrophobized silica	92
Polysulfidic-silane compound on silica	16

Rubber composition for tread of pneumatic tire:⁹²⁶

Solution SBR (styrene 32%, vinyl 42)	120 parts
Carbon black	80
Aromatic oil	12
Stearic acid	2
Zinc oxide	2
Antioxidant	0.7
Phenolic resin (CRJ-418)	25
Accelerator CZ	3.5
Accelerator (Thiram)	0.25
Sulfur	0.85

13.31 TOYS

A. MARCILLA, J.C. GARCÍA, AND M. BELTRAN
Chemical Engineering Department, Alicante University, Spain

The toxicity and the likely health risks of plasticized polymers is an important consideration in the case of toys. Plasticized PVC is the most frequently used in the production of flexible toys, thus findings on PVC parallel assessments of toxicity of toys.

There is no evidence which may indicate that there is a health risk associated with polyvinylchloride. According to the International Agency for Research on Cancer, the polymer is classified in the group 3 (not classified as carcinogenic agent in humans). Prof. Maltoni of the Oncology Institute of the University of Bologna carried out experiments on mice which were fed with a suspension of PVC in olive oil.⁹⁴⁸ After one year, this diet was stopped and the mice were kept in laboratory until their natural death. Their vital organs were then studied with no carcinogenic effect of PVC detected.

Plasticizers were subjected to a large number of research works in the last 20 years, with special attention given to plasticizers which are the most frequently used such as di-(2-ethylhexyl) phthalate, DOP, diisononyl phthalate, DINP, and di-(2-ethylhexyl) adipate, DOA.

Table 13.1 shows that DOP is one of the least toxic substances even less toxic than salt or ethyl alcohol. But works of NTP/NCI⁹⁴⁹ (National Toxicology Program, U.S.A.) found an increase in the number of mice suffering from liver cancer when they were exposed to very high levels of plasticizer. The extrapolation to adult human projects amounts higher than the actual amounts extractable from a plasticized PVC product by its contact with the saliva or typical simulating liquids. Similar results were obtained by IARC (International Agency for Research on Cancer) which led to classification of DOP as “possibly carcinogenic for humans”, as opposed to DOA, considered as non-carcinogenic for humans.

Table 13.1. Lethal dose and relative classification of some substances (Source: The Merck Chemical Products Database Chemdat and NTP, National Toxicology Program, USA)

Category	Substance	Lethal oral dose, mg/kg
Very toxic	2,3,7,8-Tetrachlorodibenzo-p-dioxin	0.020
	Potassium cyanide	5
	Arsenic oxide	20
Toxic	Sodium nitrite	85
	5-Ethyl-5-phenylbarbituric acid	162
Harmful	Oxalic acid	375
	Carbon tetrachloride	1770
Not classified as harmful	Sodium chloride	3000
	Ethanol	7060
	DOP	30600

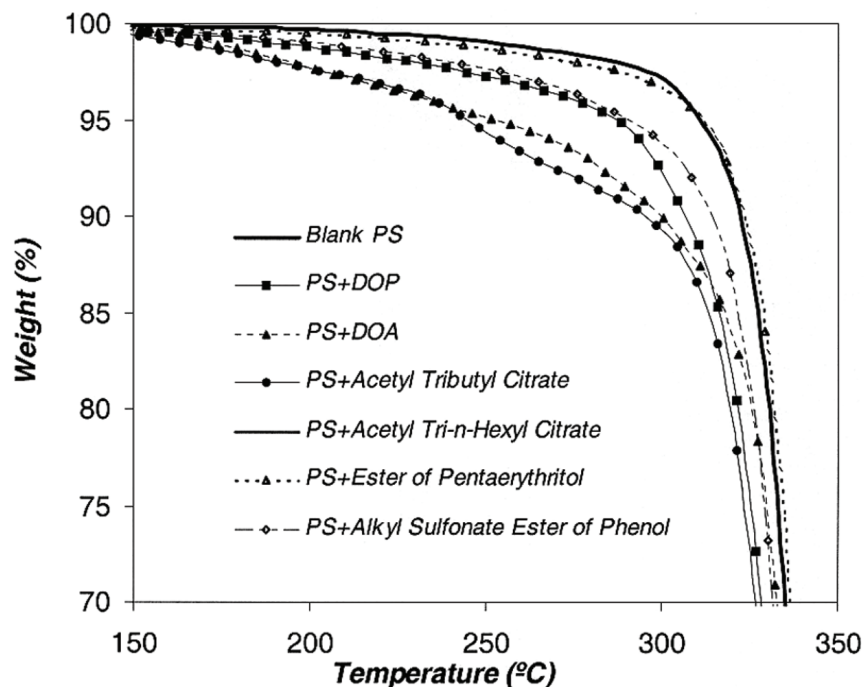


Figure 13.18. Thermogravimetric curves for PS samples aged with specimens containing 60 phr of different plasticizers.

IARC decided to extend the studies on mice to other mammals, including humans. Although DOP provoked cancer in mice, the results published in 2000⁹⁵⁰ showed that the same effect was not observed in the human tissues. The results of study⁹⁵⁰ contributed to re-qualification of DOP which was then included in the group containing substances “not classified as carcinogenic”. Identical results were obtained again for DOA.⁹⁵⁰

13.31.1 MIGRATION OF PLASTICIZERS

Low molecular weight plasticizers migrate from flexible PVC towards other surfaces in contact. There are different tests to evaluate such process. According to ASTM D 2134⁹⁵¹ two sheets, one of PVC and another of nitrocellulose, are kept in contact followed by determination of nitrocellulose hardness.

Polystyrene, PS, and acrylonitrile-butadiene-styrene polymer, ABS, were also used. Figure 13.18 shows that plasticizers considered as potential alternatives to DOP have extensive migration when contacted with PS. The amount of migrated plasticizer was determined by thermogravimetric analysis by recording two successive steps in the weight loss curves, corresponding respectively to the plasticizer release and PS degradation. The magnitude of the first weight loss can be employed as a quantitative measure of plasticizer migration.

Although this type of test can be used to study plasticizer migration from a PVC product into other objects in contacts (for example, from electric cable to a PS box or from a toy into mechanism or decorative item), there are some cases which are difficult to study

as for example the likelihood of plasticizer migration from teething rings or other flexible PVC items potentially chewed by children.

In late 1990s, the migration of plasticizers, mainly phthalates, from toys has given rise to one of the most controversial chapters in the history of PVC. The migration of phthalates, considered up to now by several ecological organizations as very dangerous chemicals, caused strong social pressure against the utilization of these plasticizers. In 1997, the Danish Government asked the European Union to take measures against the commercialization of certain teething rings produced from PVC plasticized with phthalates. PVC migration was determined using a method suggested by the European Normalization Committee. Results obtained had very significant differences between participating laboratories.

In 1998, the CSTE (Committee on Toxicity, Ecotoxicity and the Environment) issued a report in which risk of using phthalates and the limiting values were established.⁹⁵² As the first measure, all European countries were invited to guarantee the safety levels indicated in the report at the same time when laboratories throughout Europe began to work to find reliable and reproducible tests which can simulate the plasticizer extraction. In most cases, the PVC items were immersed and kept in saliva simulants for a certain time with the use of different types of agitation. All proposed methods can be classified as static or dynamic methods⁹⁵² (for example, the set up by the Laboratory of the Government Chemist, U.K. is static and the method of Toy Technological Institute AIJU in Spain can be classified as dynamic). The main differences between the different methods are in shape and weight of a sample, the method of agitation, composition of saliva solution, duration and temperature of exposure, and the method of determination of the extracted plasticizer.

Also, different methods have been used to simulate the chewing process and its intensity, such as magnetic agitation, ultrasonic agitation, or even agitation in a rotating cylinder with agate pieces. As it can be expected,⁹⁵² the extraction results varied widely but formed the following relationship: static method < dynamic method < chewing extraction.

In December 1998, Greek Minister C. Papanikolaou announced the intention to ban PVC toys for children under three years old. Other countries including Netherlands, Norway, and Finland followed.

The polemic also spread out to U.S.A., where the Vice President decided to order a rigorous investigation regarding the health effects of flexible PVC. Results obtained by the American Council on Science and Health were published in June 1999.⁹⁵³ The use of DINP in toys was favored: "...Based on its review of available scientific data and exposure estimates for DINP, the Panel concludes that DINP in flexible toys is unlikely to pose a health risk to children...". In spite of all the work done so far various associations show little confidence in reports, arguing that scientist may have been influenced by PVC manufacturers.

Under these popular pressures, manufacturers began to look for alternative plasticizers. CSTE does not support use of other alternative plasticizers because there is not enough data on the health risks of citrates and adipates considered as potential replacements.⁹⁵⁴ Moreover, it was found that reliable method of analysis of the amount of plasticizer migration does not exist and cannot be used with legislative purpose in mind.⁹⁵⁵

Finally, in December 1999 the European Union decided to ban the commercialization of flexible PVC toys for children less than 3 years old containing DOP, DINP, di-n-octyl phthalate, DNOP, and benzyl butyl phthalate, BBP.⁹⁵⁶ DOP (DEHP) is not permitted for toys manufacturing and in view of the latter regulations, it is not expected to be in the future. According to the Commission Communication C/2008 34/1 published on February 7 2008, it is stated that: "As regards consumer use of DEHP, the existing legislative measures for consumer protection, in particular the provisions under Council Directive 76/769/EEC (6) (marketing and use Directive) as regards CMR substances and Directive 2005/84/EC of the European Parliament and of the Council (7) on phthalates in toys and child care articles are considered sufficient to address risks identified to consumers." In the Directive 2005/84/EC it is indicated that DEHP, DBP and BBP shall not be used as substances or as constituents of preparations, at concentrations of greater than 0.1% by mass of the plasticized material, in toys and childcare articles. Such toys and childcare articles containing these phthalates in a concentration greater than the limit mentioned above shall not be placed on the market.

13.31.2 SUBSTITUTES TO PHTHALATES

There are less common plasticizers in the market which potentially may be used as phthalate replacements. Some of these plasticizers have been widely used in PVC manufacturing, such as adipates, while others have been only used for specific purposes, mostly because of their higher price in comparison to phthalates. These plasticizers may belong to the following chemical groups:

- 1,2-Cyclohexane dicarboxylic acid, diisononyl ester
- Phosphoric esters
- Citric esters, such as acetyl tributyl citrate, ATBC
- Esters of aliphatic acids, such as adipates or sebacates, DOA, diisooctyl adipate, DIOA, diisononyl adipate, DINA, diisodecyl adipate, DIDA, dibutyl sebacate, DBS, di-(2-ethylhexyl) sebacate, DOS, and diisooctyl sebacate, DIOS
- Benzoates
- Terephthalate of bis-(2-ethylhexyl)
- Trimellitic esters, such as tri-(2-ethylhexyl) trimellitate, TOTM, triisooctyl trimellitate, TIOTM, triisononyl trimellitate, TNTM
- Polymeric esters

Toxicological and carcinogenic aspects are very important for plasticizers destined to be used in toy manufacture but they are not known at this time for most of these plasticizers to ensure their safe use in this application. Presently known facts seem to indicate that some of the plasticizers may be potentially useful to replace phthalates. A report prepared for the European Commission Directorate-General Enterprise⁹⁵⁷ indicates a lower health risk with acetyl tributyl citrate (ATBC). It was also reported that the substitution of phthalates by benzoates (such as diethylene glycol dibenzoate), alkylsulfonic phenyl esters, and possibly some adipates, Trimellitites, sebacates and azelates should reduce health hazards; however it is also recognized that the information available for DOA and ATBC is much less extensive than that available for phthalates.

More recently, a study by EPA (Environmental Protection Agency) in the USA, dated on November 2001, has revealed that isodecyl benzoate does not pose an unacceptable risk to human health.⁹⁵⁸ In this respect, it is also worth mentioning a report issued by

the Danish EPA in 2001,⁹⁵⁹ in which different plasticizers are recommended for different purposes. Table 13.2 points out to substitute phthalates in toys by a derivative of citric acid and contains many other suggestions.

Table 13.2. Phthalate substitutes⁹⁵⁹

Name of substitute	Expected most relevant application
Di-(2-ethylhexyl) phosphate	Cables
Tri-(2-ethylhexyl) phosphate	Cables
Tri-(2-ethylhexyl) trimellitate	Cables
Alkyl sulfonic acid ester	Cables
Di-(2-ethylhexyl) adipate	Flooring and wall coverings
Butane ester (2,2,4-trimethyl-1,3-pentanediodiisobutyrate)	Flooring and wall coverings
Epoxidized soybean oil	Lacquers and paints
Acetyl tributyl citrate	Toys
Dioctyl sebacate	Printing inks

It is pertinent that phthalate substitution for certain toys and children care items is still in progress because further studies concerning toxicological and technical aspects of their substitutes are still required to confirm selection of substitutes. This is still a big issue now and it is expected that more information will be available in future.

13.32 TUBING

13.32.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) adipate in coextruded tubing⁹⁶⁰
- di-(2-ethylhexyl) phthalate in coextruded tubing⁹⁶⁰
- diisodecyl phthalate in multilayer tubing having electrostatic dissipation for handling hydrocarbon fluids^{961,962}
- Aliphatic diester of C16-30 dicarboxylic acid in flexible PVC⁹⁷⁰
- tri-(2-ethylhexyl) trimellitate in flexible medical products^{964,966,969}
- epoxidized soybean oil in multilayer tubing having electrostatic dissipation for handling hydrocarbon fluids,^{961,962} in medical tubing,⁹⁶⁴ and in thrombo-resistant plastic article⁸⁴⁴
- mineral oil in flexible tubing material⁹⁷¹

13.32.2 PLASTICIZER CONCENTRATION

- diisodecyl phthalate: 1 to 13 wt% in multilayer tubing having electrostatic dissipation for handling hydrocarbon fluids^{961,962}
- tri-(2-ethylhexyl) trimellitate: 43 to 57 wt% in flexible medical products manufactured from ultrahigh molecular weight PVC^{964,966,969}

13.32.3 REASONS FOR PLASTICIZER USE

- to render mixture flexible^{963,964}
- improvement of processability⁹⁶⁷

- improvement of electric conductivity⁹⁶⁷
- limiting migration⁹⁶⁰

13.32.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- two or three layers are created each containing the same concentration but different type of plasticizer (e.g., di-(2-ethylhexyl) adipate and di-(2-ethylhexyl) phthalate. Di-(2-ethylhexyl) adipate is in the outer layer because it is considered less toxic in this medical application. Equal concentrations are believed to prevent interlayer migration⁹⁶⁰

Disadvantages

- low molecular weight plasticizers may be extracted by fluid passing tubing⁹⁶³
- di-(2-ethylhexyl) phthalate leaches out of tubing to body liquids (e.g., blood) in contact⁹⁶⁴
- di-(2-ethylhexyl) phthalate leaches out during steam sterilization⁹⁶⁸
- di-(2-ethylhexyl) phthalate contributes to smoke during welding⁹⁶⁸

13.32.5 EXAMPLES OF FORMULATIONS

Flexible medical products:⁹⁶⁴

PVC resin (UHMW)	100 phr
Tri-(2-ethylhexyl) trimellitate	120
Epoxidized soybean oil	5
Calcium-zinc stabilizer	0.32
Mineral oil	0.2

13.33 WIRE AND CABLE

13.33.1 PLASTICIZER TYPES

- di-(2-ethylhexyl) phthalate in electric cable insulation,⁸⁵ in wire coating,⁹⁸⁴ and in plenum cable⁹⁹⁷
- diisodecyl phthalate in cable jacket⁹⁷⁷ and in insulated wire⁹⁸⁹
- ditridecyl phthalate in wire insulation⁹⁹⁵
- C₇ to C₉ phthalate (Palatinol 79) in low smoke, flame retardant cable⁹⁹⁴
- C₉ to C₁₁ phthalate (Palatinol 911) in automotive cable⁹⁸³
- tri-(2-ethylhexyl) trimellitate in wire insulation,⁹⁷² in wire and cable product,⁹⁹⁰ and in plenum cable⁹⁹⁷
- triisononyl trimellitate in plenum cables⁹⁹² and in low smoke, flame retardant cable⁹⁹⁴
- isodecyl diphenyl phosphate in plenum cable⁹⁹² and in flame retardant composition⁹⁹⁵
- tricresyl phosphate in wire coating⁹⁸³
- epoxidized soybean oil in cable jacket⁹⁷⁷
- glycerin in superconducting wires made out of ethyl cellulose⁹⁸⁷
- paraffin oil in plasticization of ethylene-propylene-diene terpolymer^{982,988}
- polyester plasticizer (Paraplex G-31) in wire insulation⁹⁷²
- adipic polymeric plasticizer (Palamoll 652) in automotive cable⁹⁸³

13.33.2 PLASTICIZER CONCENTRATION

- di-(2-ethylhexyl) phthalate: 5 to 20 wt% in plenum cable⁹⁹⁷ and cable insulation^{1000,1001,1002}
- diisodecyl phthalate: 40 phr (25 wt%) in insulated wire⁹⁸⁹
- ditridecyl phthalate: 58 phr in wire insulation⁹⁷²
- tri-(2-ethylhexyl) trimellitate: 56 phr in wire insulation⁹⁷² and 5 to 20 wt% in plenum cable⁹⁹⁷
- polyester plasticizer (Paraplex G-31): 64 phr in wire insulation⁹⁷²

13.33.3 REASONS FOR PLASTICIZER USE

- electrical grade⁹⁷²
- good heat aging characteristics⁹⁷²
- improved flexibility^{978,980,986}
- improved processing⁹⁸⁰
- reduced minimum required processing temperature⁹⁸⁰
- low freezing temperature⁹⁸³
- reduced melt viscosity⁹⁸⁰

13.33.4 ADVANTAGES AND DISADVANTAGES OF PLASTICIZERS USE

Advantages

- epoxidized soybean oil helps in better color retention⁹⁷⁷

Disadvantages

- plasticizer migration to optical fiber coating may result in decreased coating adhesion and possible delamination⁹⁷⁶
- leaching of plasticizer may cause degradation of properties of encapsulated fiber in telecommunication cable⁹⁸⁵
- when diisooctyl phthalate was used in telecommunication cable strip force was reduced by 90% after 6 months aging at 85°C compared with 35% reduction after 45 days of aging at 110°C when tri-(2-ethylhexyl) trimellitate was used as a plasticizer⁹⁸⁵
- plasticizers emitted from automotive wires contribute to fogging⁹⁸⁶
- addition of plasticizer usually increases flammability⁹⁹²
- migration of plasticizer between outer and inner insulation changes dielectric properties and shortens useful life of cable⁹⁹⁵

13.33.5 EFFECT OF PLASTICIZERS ON PRODUCT PROPERTIES

Study of electric cable used for 18 years outdoors in Romania shows that only 2% of original quantity of di-(2-ethylhexyl) phthalate has been lost during service life. Formulation was stabilized with lead stabilizer. Twenty percent of original stabilizer was used and required replacement in recycling process.⁹⁷⁴

A similar study in Sweden (see formulation in the next section) showed that only 1% of extractable matter was lost during 30-40 years of cable use, material was thermally stable, and mechanical performance measured by elongation changed very little. Experimental studies conducted in laboratory which simulated service life by thermal aging at 80°C and considering activation energy in Arrhenius equation at 95 kJ/mol showed that cables should perform for at least 44 years. The cables collected from field are suitable for recycling with minimal adjustments to formulation. Figure 13.19 shows that stability of insula-

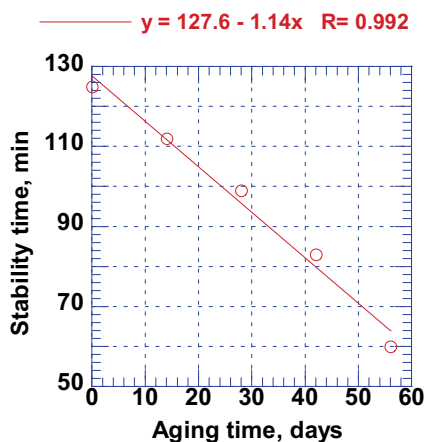


Figure 13.19. Stability of PVC plasticized with 55 phr of di-(2-ethylhexyl) phthalate vs. aging time at 90°C. [Data from Jakubowicz I; Yarahmadi N; Gevert T, *Polym. Deg. Stab.*, **66**, No.3, 1999, p.415-21.]

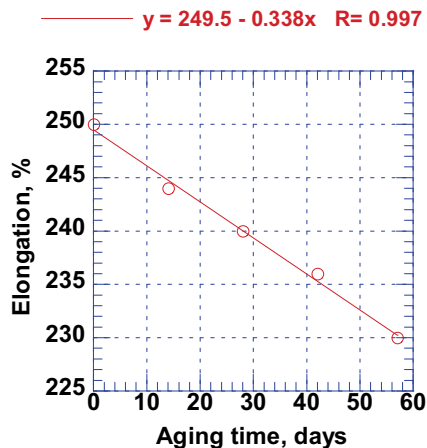


Figure 13.20. Elongation of PVC plasticized with 55 phr of di-(2-ethylhexyl) phthalate vs. aging time at 90°C. [Data from Jakubowicz I; Yarahmadi N; Gevert T, *Polym. Deg. Stab.*, **66**, No.3, 1999, p.415-21.]

tion has linear relationship with duration of aging. Figure 13.20 shows that changes in elongation are very small.⁹⁷⁵

Polyolefin and PVC insulated cable were subjected to aging at 80°C for 16.5 weeks.⁹⁹⁹ Mass loss from polyolefin coated wire was 0.21% and for PVC coated 0.38%. In PVC coated cable, migration of plasticizer to sheath was apparent with about 5% plasticizer involved.⁹⁹⁹

Extensive aging studies have been recently conducted, showing that PVC cable are thermally resistant.¹⁰⁰¹⁻¹⁰⁰²

13.33.6 EXAMPLES OF FORMULATIONS

Wire insulation compound:⁹⁷²

PVC	100 parts
Tri-(2-ethylhexyl) trimellitate	56
Electrical grade clay	7
Dibasic lead phthalate	10
Dibasic lead stearate	0.25
Bisphenol A	0.3

Wire insulation compound:⁹⁸⁹

PVC	100 parts
Diisodecyl phthalate	40
Calcium carbonate	15
Ca-Zn stabilizer	1.5
Hydrotalcite	3.5
Stearic acid	0.1

Flame retardant plasticized PVC:⁹⁸¹

PVC resin (Geon 30)	100 parts
Antimony trioxide	15
Trioctyl trimellitate (Uniplex 546-A)	34.3
Lead stabilizer	5
Diocetyl tetrabromophthalate (Uniplex FRP-45)	30
Diocetyl tetrachlorophthalate (Uniplex FRP-27)	10

Flame retardant cable jacketing and wire insulation:⁹⁹⁵

PVC	100 parts
Pentaerythritol ester plasticizer (Hercoflex 707A)	33
Calcined clay (SP33, electrical grade)	5
Aluminum trihydrate (Alcoa C710B)	70
Basic lead heat stabilizer (Lectro 90 TA)	6
Stearic acid	0.25
Antimony trioxide (Fireshield LSFR)	5
Brominated phthalate ester (great Lakes DP45)	10
Isodecyl diphenyl phosphate	5
Ammonium octamolybdate flame retardant	10
Zinc borate flame retardant	2

Cable jacket of plenum cable:⁹⁹²

PVC (Geon 855)	70 parts
CPVC (Temperite 674)	30
Isodecyl diphenyl phosphate	16
Molybdenum oxide	4
Hydrate alumina (e.g., Micral 932)	90
Dibasic lead phthalate	8
Antimony trioxide	4
Ethylene acrylic elastomer (Vamac G)	45
Irganox 1010	0.3
Zinc borate	7
Triisononyl trimellitate (Jayflex TINTM)	7
Lubricant (Struktol TRO16)	2
Aluminum silicate (Whitex clay)	15

Cable insulation formulation used in Sweden in 1974:⁹⁷⁵

PVC	49 wt%
Calcium carbonate	18
Lead sulfate or stearate	2.5
Antimony trioxide	1.5
Chlorinated paraffins	12
Di-(2-ethylhexyl) phthalate	17

REFERENCES

- 1 Lear J; Lawrey B; Barksby N; Hinney H, Polyurethanes Expo '99. Conf. proc., American Plast. Council, Alliance for the Polyurethanes Ind., Orlando, Fl., 12th-15th Sept.1999, p.69-78.
- 2 Dillard J; Ward T; Morgan J, *Pittura Vernici*, **75**, No.16, 1st-15th Oct.1999, p.72-5.
- 3 *Machine Design*, **70**, No.19, 22nd Oct.1998, p.124/6.
- 4 Arendt W D, *Adhesives Age*, **39**, No.9, Aug.1996, p.37-8.
- 5 Seghal K; Bassett D R, Euradh '94. Conf. proc., Societe Francaise du Vide; Institute of Mater.; Dechema Institut, Mulhouse, 12th-15th Sept.1994, p.203-7.
- 6 Gardiner J, *Eur. Adhesives & Sealants*, **12**, No.1, March 1995, p.4/6.
- 7 Bowtell M, *Adhesives Age*, **38**, No.5, May 1995, p.56/9.
- 8 **US Patent** 6,495,628.
- 9 **US Patent** 6,469,122.
- 10 **US Patent** 6,469,082.
- 11 **US Patent** 6,465,557.
- 12 **US Patent** 6,457,294.
- 13 **US Patent** 6,455,598.
- 14 **US Patent** 6,452,873.
- 15 **US Patent** 6,451,441.
- 16 **US Patent** 6,441,092.
- 17 **US Patent** 6,429,244.
- 18 **US Patent** 6,416,858.
- 19 **US Patent** 6,414,077.
- 20 **US Patent** 6,413,354.
- 21 **US Patent** 6,410,640.
- 22 **US Patent** 6,410,627.
- 23 **US Patent** 6,403,685.
- 24 **US Patent** 6,391,993.
- 25 **US Patent** 6,391,415.
- 26 **US Patent** 6,383,324.
- 27 **US Patent** 6,380,292.
- 28 **US Patent** RE37,683.
- 29 **US Patent** 6,375,977.
- 30 **US Patent** 6,355,344.
- 31 **US Patent** 6,348,210.
- 32 **US Patent** 6,342,561.
- 33 **US Patent** 6,329,468.
- 34 **US Patent** 6,322,650.
- 35 **US Patent** 6,319,982.
- 36 **US Patent** 6,300,400.
- 37 **US Patent** 6,297,324.
- 38 **US Patent** 6,296,730.
- 39 **US Patent** 6,291,571.
- 40 **US Patent** 6,291,562.
- 41 **US Patent** 6,291,557.
- 42 **US Patent** 6,290,871.
- 43 **US Patent** 6,290,803.
- 44 **US Patent** 6,288,149.
- 45 **US Patent** 6,280,557.
- 46 **US Patent** 6,274,165.
- 47 **US Patent** 6,232,366.
- 48 **US Patent** 6,231,883.
- 49 **US Patent** 6,218,457.
- 50 **US Patent** 6,218,005.
- 51 **US Patent** 6,211,425.
- 52 **US Patent** 6,207,272.
- 53 **US Patent** 6,204,321.
- 54 **US Patent** 6,194,498.
- 55 **US Patent** 6,187,850.
- 56 **US Patent** 6,184,285.

- 57 US Patent 6,180,242.
- 58 US Patent 6,172,156.
- 59 US Patent 6,152,868.
- 60 US Patent 6,162,858.
- 61 US Patent 6,133,398.
- 62 US Patent 6,106,940.
- 63 US Patent 6,090,867.
- 64 US Patent 6,087,425.
- 65 US Patent 6,080,480.
- 66 US Patent 6,077,925.
- 67 US Patent 6,077,895.
- 68 US Patent 6,069,188.
- 69 US Patent 6,068,852.
- 70 US Patent 6,054,213.
- 71 US Patent 6,051,748.
- 72 US Patent 6,042,678.
- 73 US Patent 6,034,168.
- 74 US Patent 6,034,159.
- 75 US Patent 6,008,148.
- 76 US Patent 5,993,849.
- 77 US Patent 5,993,530.
- 78 US Patent 5,989,522.
- 79 US Patent 5,983,593.
- 80 US Patent 5,976,305.
- 81 US Patent 5,973,028.
- 82 US Patent 5,969,025.
- 83 US Patent 5,948,853.
- 84 US Patent 5,948,433.
- 85 US Patent 5,947,127.
- 86 US Patent 5,947,126.
- 87 US Patent 5,939,483.
- 88 US Patent 5,922,809.
- 89 US Patent 5,932,639.
- 90 US Patent 5,866,651.
- 91 US Patent 5,852,103.
- 92 US Patent 5,849,266.
- 93 US Patent 5,827,393.
- 94 US Patent 5,792,303.
- 95 US Patent 5,786,418.
- 96 US Patent 5,753,724.
- 97 US Patent 5,747,573.
- 98 US Patent 5,695,779.
- 99 US Patent 5,688,845.
- 100 US Patent 5,681,517.
- 101 US Patent 5,672,677.
- 102 US Patent 5,672,652.
- 103 US Patent 5,668,209.
- 104 US Patent 5,631,318.
- 105 US Patent 5,627,229.
- 106 US Patent 5,608,028.
- 107 US Patent 5,583,187.
- 108 US Patent 5,571,860.
- 109 US Patent 5,534,053.
- 110 US Patent 5,519,072.
- 111 US Patent RE35,144.
- 112 Baoyan Zhang; Huimin Tan, *Eur. Polym. J.*, **34**, Nos.3-4, March/April 1998, p.571-5.
- 113 Shashoua Y, *Polym. Preprints*, **41**, 2, 2000, p.1796-7.
- 114 US Patent 6,494,972.
- 115 US Patent 6,486,268.
- 116 US Patent 6,458,227.

- 117 **US Patent** 6,437,034.
118 **US Patent** 6,372,849.
119 **US Patent** 6,322,848.
120 **US Patent** 6,232,401.
121 **US Patent** 6,027,767.
122 **US Patent** 5,866,651.
123 **US Patent** 5,851,591.
124 **US Patent** 5,849,832.
125 **US Patent** 5,840,797.
126 Wypych G, **Handbook of Material Weathering**. 3rd Ed., *ChemTec Publishing*, Toronto, 2003.
127 Georgeau P C, Muldel L A, **US Reissued Patent US RE41,586 E**, *Chem Link Inc.*, Aug. 24 2010.
128 Kettner M R, Stimpson M J, Holt M S, Whitson R L, Pont D, **US Patent Application Publication US 2008/0057317**, *Eastman*, Mar. 6, 2008.
129 Kho D H, Cho H J, Chang K, Kim S, Baek J, **US Patent Application Publication US 2011/0003091**, *LG Chem. Ltd.*, Jan. 6, 2011.
130 Koike M, Hara S, Ichikawa H, **US Patent Application Publication US 2010/0129653**, *Yazaki Corp.*, May 27, 2010.
131 Etoh H, Tetsumoto T, **US Patent Application Publication US 2009/02911300**, *Lintec Corp.*, Nov. 26, 2009.
132 Gu J-D, *Int. Biodet. Biodeg.*, **59**, 170-79, 2007.
133 Reyes A M, Short J R, Randazzo S, **US Patent Application Publication US 2006/0278338**, *PPG Industries*, Dec.14, 2006.
134 Kato H, Matsumoto K, Hirose T, **US Patent Application Publication US 2008/0119620**, *IP Group*, May 22, 2008.
135 Reyes A M, Short J R, Randazzo S, **US Patent Application Publication US 2011/0143028**, *PPG Industries*, Jun. 16, 2011.
136 **US Patent** 6,468,561.
137 **US Patent** 6,395,760.
138 Takenaka A, Nomoto S, **US Patent Application Publication US 2008/0262150**, *Kao Corporation*, Oct. 23, 2008.
139 Nigen; Tandon P, *Kunststoffe Plast. Europe*, **85**, No.9, Sept.1995, p.51-3.
140 *Modern Plast. Intl.*, **28**, No.10, Oct.1998, p.233.
141 Ellul M D, *Rubber Chem. Technol.*, **71**, No.2, May/June 1998, p.244-76.
142 Voskanyan P S; Sarkisyan M B; Mkhitaryan M A; Badalyan V E, *Intl. Polym. Sci. Technol.*, **22**, No.10, 1995, p.T/1-3.
143 Mann D, *Automotive Engineer*, 21, No.2, April/May 1996, p.23-4.
144 **US Patent** 6,472,042.
145 **US Patent** 6,462,113.
146 **US Patent** 6,429,244.
147 **US Patent** 6,337,374.
148 **US Patent** 6,329,061.
149 **US Patent** 6,315,848.
150 **US Patent** 6,255,374.
151 **US Patent** 6,166,160.
152 **US Patent** 6,119,807.
153 **US Patent** 6,103,309.
154 **US Patent** 6,077,903.
155 **US Patent** 6,057,044.
156 **US Patent** 6,042,678.
157 **US Patent** RE36,296.
158 **US Patent** 5,932,353.
159 **US Patent** 5,863,064.
160 **US Patent** 5,739,184.
161 **US Patent** 5,723,520.
162 **US Patent** 5,710,199.
163 Chien Y-C, *Sci. Total Environ.*, **382**, 228-39, 2007.
164 Chapman B R, Valentage J, Hill J M, Lundmark B R, **US Patent 8,003,725 B2**, *ExxonMobil*, Aug. 23, 2011.
165 Ikeda Y, Kashiwamura T, Takeuchi K, **US Patent 8,017,677, B2**, *Idemitsu Kosan Co., Ltd.*, Sep. 13, 2011.
166 Nishino R, Uejou H, **US Patent 6,769,453**, *Piolar Inc.*, Aug. 3, 2004.

- 167 Nakatsu A, Manai R, **US Patent Application Publication US 2007/0110938**, *Nitta Moore Co.*, May 17, 2007.
- 168 Gardner J A, **US Patent 7,247,382 B2**, *Magna Interior Systems Inc.*, Jul. 24, 2007.
- 169 Billast K M D B, **US Patent Application Publication US 2009/0130316**, *Ferro*, May 21, 2009.
- 170 Mitsudera T, Iwanami K, Nishihara K, **US Patent Application Publication**, Mar. 6, 2006.
- 171 Tansey W J, **US Patent Application Publication US 2011/0028625**, *International Automotive Components Group North America*, Feb. 3, 2011.
- 172 Al-Noaimi K K; El-Hosiny F I; Abo-El-Enein S A, *J. Thermal Analysis Calorimetry*, **61**, No.1, 2000, p.173-80.
- 173 Tantawi S H, *Polym. Plast. Technol. Eng.*, **36**, No.6, 1997, p.863-72.
- 174 Sumathy C T; Dharakumar M; Devi M S; Saccubai S, *J. Appl. Polym. Sci.*, **63**, No.10, 7th March 1997, p.1251-7.
- 175 Kaspar H R E; Pizzi A, *J. Appl. Polym. Sci.*, **59**, No.7, 14th Feb.1996, p.1181-90.
- 176 Ray I; Gupta A P; Biswas M, *Cement Concrete Composites*, **17**, No.1, 1995, p.9-21.
- 177 El-Hosiny F I; Gad E A M, *J. Appl. Polym. Sci.*, **56**, No.2, 11th April 1995, p.153-9.
- 178 Ray I; Gupta A P; Biswas M, *Cement Concrete Composites*, **16**, No.4, 1994, p.309-16.
- 179 **US Patent** 6,488,792.
- 180 **US Patent** 6,441,054.
- 181 **US Patent** 6,355,191.
- 182 **US Patent** 6,073,410.
- 183 **US Patent** 6,035,591.
- 184 **US Patent** 5,997,630.
- 185 **US Patent** 5,968,257.
- 186 **US Patent** 5,948,157.
- 187 **US Patent** 5,843,222.
- 188 **US Patent** 5,753,037.
- 189 **US Patent** 5,641,584.
- 190 Vikan H, Justnes H, Winnefeld F, Figi R, *Cement Concrete Res.*, **37**, 1502-11, 2007.
- 191 Emoto T, Bier T A, *Cement Concrete Res.*, **37**, 647-54, 2007.
- 192 Clemente P, Ferrari G, Gamba M, Pistolesi C, Squinzi M, Surico F, Badesso L, **US Patent Application Publication US 2007/0151486**, Jul 5. 2007.
- 193 Wypych J, **Polymer Modified Textile Materials**, *John Wiley & Sons*, New York, 1988.
- 194 Carow I, *Polym. Preprints*, **41**, 2, 2000, p.1800-1.
- 195 Monney L; Jamois-Tasserie M; Dubois C; Villa F; Lallet P; Renaud C, *Polym. Deg. Stab.*, **72**, No.3, 2001, p.459-68.
- 196 Zadhoush A; Alsharif M A, *J. Industrial Text.*, **30**, No.1, July 2000, p.50-62.
- 197 Hoefler R, *Eur. Coat. J.*, No.3, 2000, p.26/37.
- 198 Arendt W D; Lang J, Antec '98. Volume III. Conf. proc., SPE, Atlanta, Ga., 26th-30th April 1998, p.3278-83.
- 199 **US Patent** 6,319,969.
- 200 **US Patent** 6,287,679.
- 201 **US Patent** 6,238,772.
- 202 **US Patent** 6,187,837.
- 203 **US Patent** 6,171,984.
- 204 **US Patent** 6,120,784.
- 205 **US Patent** 6,017,586.
- 206 Weber R F, Zagryn M, **US Patent Application Publication US 2008/0171482**, *L&P Property Management Company*, Jul. 17, 2008.
- 207 Guelcher S A, Bhattacharyya S, Zienkiewicz J K, Tanner S A, Dumas J E, **US Patent Application Publication US 2010/0112032**, May 6 2010.
- 208 Barbier J, Dever C, Soum S, **US Patent Application Publication US 2010/0256264**, *Valagro Carbone Renouvelable Poitou-Charentes*, Oct. 7, 2010.
- 209 Wintebottom J, Kaes D R, Tunc D C, Boyce T M, Knaack D, Russell J, Bhattacharyya S, **US Patent Application Publication US 2007/0191963**, Aug. 16, 2007.
- 210 Korzhenko A, Brule B, Chiquot A, Piccione P M, Miaudet P, Merceron A, **US Patent Application Publication US 2011/0201731**, *Arkema France*, Aug. 18, 2011.
- 211 **US Patent** 6,485,731.
- 212 **US Patent** 6,413,526.
- 213 **US Patent** 6,395,263.
- 214 **US Patent** 6,391,938.

- 215 **US Patent** 6,387,356.
216 **US Patent** 6,361,782.
217 **US Patent** 6,346,255.
218 **US Patent** 6,342,561.
219 **US Patent** 6,342,209.
220 **US Patent** 6,312,676.
221 **US Patent** 6,306,375.
222 **US Patent** 6,299,891.
223 **US Patent** 6,280,756.
224 **US Patent** 6,280,747.
225 **US Patent** 6,254,876.
226 **US Patent** 6,203,809.
227 **US Patent** 6,203,806.
228 **US Patent** 6,203,780.
229 **US Patent** 6,197,316.
230 **US Patent** 6,190,677.
231 **US Patent** 6,165,457.
232 **US Patent** 6,159,486.
233 **US Patent** 6,136,300.
234 **US Patent** 5,993,834.
235 **US Patent** 5,976,521.
236 **US Patent** 5,965,116.
237 **US Patent** 5,965,116.
238 **US Patent** 5,945,095.
239 **US Patent** 5,929,173.
240 **US Patent** 5,811,109.
241 **US Patent** 5,753,243.
242 **US Patent** 5,747,017.
243 **US Patent** 5,709,850.
244 **US Patent** 5,578,297.
245 Amberg-Mueller J P, Hauri U, Schlegel U, Hohl C, Brueschweiler B J, *J. Verbr. Lebensm.*, **5**, 429-42, 2010.
246 Kim C-H, Ko T-S, Kim H-J, Kim C-J, Choi J-H, Ji C-H, **US Patent Application Publication US 2011/0165208**, Jul. 7, 2011.
247 Bandres M, Deswartvaegher A, De Caro P, Senet J-P, Roux S T, **US Patent Application Publication US 2010/0158835**, *Durlin France*, Jun. 24, 2010.
248 Mu W, McKenna L C, Stepniewski G J, Luo D, Naza S, Wang T X, **US Patent Application Publication US 2011/0073126**, Mar.51, 2011.
249 East A, **US Patent Application Publication US 2007/0282042**, Dec. 6, 2007.
250 Csefalvayova L, Strlic M, Karjalainen, *Anal. Chem.*, **83**, 5101-6, 2011.
251 Dental drugs - gels deliver the goods, *Mater. World*, **7**, No.10, Oct.1999, p.610-2.
252 Parker S; Martin D; Braden M, *BioMater.*, **20**, No.1, Jan.1999, p.55-60.
253 Decker C; Bendaikha T, *J. Appl. Polym. Sci.*, **70**, No.11, 12th Dec.1998, p.2269-82.
254 **US Patent** 6,482,395.
255 **US Patent** 6,441,354.
256 **US Patent** 6,403,671.
257 **US Patent** 6,340,477.
258 **US Patent** 6,335,413.
259 **US Patent** 6,306,785.
260 **US Patent** 6,251,410.
261 **US Patent** 6,197,331.
262 **US Patent** 6,161,555.
263 **US Patent** 6,136,886.
264 **US Patent** 6,133,339.
265 **US Patent** 6,077,075.
266 **US Patent** 6,029,678.
267 **US Patent** 6,004,539.
268 **US Patent** 5,977,199.
269 **US Patent** 5,968,998.
270 **US Patent** 5,955,513.
271 **US Patent** 5,948,129.

- 272 **US Patent** 5,865,197.
273 **US Patent** 5,863,965.
274 **US Patent** 5,849,266.
275 **US Patent** 5,824,720.
276 **US Patent** 5,795,151.
277 **US Patent** 5,648,399.
278 **US Patent** 5,645,853.
279 **US Patent** 5,639,795.
280 **US Patent** 5,583,164.
281 **US Patent** 5,569,691.
282 Munksgaard E C, *Eur. J. Oral Sci.*, **113**, 166-69, 2005.
283 Bozek R, Koczorowski R, Rogalewicz R, Voelkel A, Czarnecka B, Nicholson J W, *Dental Mater.*, **27**, 281-90, 2011.
284 Chaves C A L, Machado A L, Carlos I Z, Giampaolo E T, Pavarina A C, Vergani C E, *Dental Mater.*, **26**, 1017-23, 2010.
285 Tanaka N, Nomura Y, Nishikiori R, Shibata S, Shirai K, Fujitani M, *J. Dent.*, **33**, 577-83, 2005.
286 Kawahara T, Nomura Y, Tanaka N, Teshima W, Okazaki M, Shintani H, *J. Dent.*, **32**, 277-283, 2004.
287 Hashiguchi M, Yamashita M, Kazama H, **US Patent 7,906,565 B2**, *Tokuyama Corp.*, Mar. 15, 2011.
288 Jia W, Jin S, **US Patent Application Publication US 2007/0049656**, *Pentron Clinical Technologies, Inc.*, Mar. 1, 2007.
289 Kim J-Y, Kim J-H, Chang S-Y, Yun S-Y, Yang H-Y, Kwak S-H, **US Patent Application Publication US 2006/0193793**, *Fox Rothschild LLP*, Aug. 31, 2006.
290 **US Patent** 5,500,208.
291 Morgan H; Foot P J S; Brooks N W, *J. Mater. Sci.*, **36**, No.22, 15th Nov. 2001, p.5369-77.
292 Nagayama N; Yoyoyama M, *Molecular Crystals Liquid Crystals*, **327**, 1999, p.19-22.
293 **US Patent** 6,492,967.
294 **US Patent** 6,485,672.
295 **US Patent** 6,482,560.
296 **US Patent** 6,472,114.
297 **US Patent** 6,465,794.
298 **US Patent** 6,452,554.
299 **US Patent** 6,421,035.
300 **US Patent** 6,410,877.
301 **US Patent** 6,375,865.
302 **US Patent** 6,342,679.
303 **US Patent** 6,340,426.
304 **US Patent** 6,337,962.
305 **US Patent** 6,337,038.
306 **US Patent** 6,327,136.
307 **US Patent** 6,283,903.
308 **US Patent** 6,297,385.
309 **US Patent** 6,266,230.
310 **US Patent** 6,248,814.
311 **US Patent** 6,246,568.
312 **US Patent** 6,224,964.
313 **US Patent** 6,187,487.
314 **US Patent** 6,171,669.
315 **US Patent** 6,100,339.
316 **US Patent** 6,078,778.
317 **US Patent** 6,071,643.
318 **US Patent** 6,071,596.
319 **US Patent** 6,064,561.
320 **US Patent** 6,031,712.
321 **US Patent** 6,031,184.
322 **US Patent** 5,993,958.
323 **US Patent** 5,991,566.
324 **US Patent** 5,982,606.
325 **US Patent** 5,982,346.
326 **US Patent** 5,977,685.
327 **US Patent** 5,977,022.

- 328 **US Patent** 5,958,594.
329 **US Patent** 5,922,268.
330 **US Patent** 5,912,436.
331 **US Patent** 5,908,682.
332 **US Patent** 5,876,647.
333 **US Patent** 5,874,184.
334 **US Patent** 5,866,284.
335 **US Patent** 5,863,626.
336 **US Patent** 5,770,821.
337 **US Patent** 5,767,826.
338 **US Patent** 5,763,069.
339 **US Patent** 5,752,130.
340 **US Patent** 5,739,801.
341 **US Patent** 5,739,742.
342 **US Patent** 5,712,334.
343 **US Patent** 5,689,771.
344 **US Patent** 5,668,070.
345 **US Patent** 5,665,500.
346 **US Patent** 5,656,371.
347 **US Patent** 5,634,179.
348 **US Patent** 5,619,311.
349 **US Patent** 5,614,044.
350 **US Patent** 5,597,661.
351 **US Patent** 5,557,496.
352 **US Patent** 5,525,208.
353 **US Patent** 5,523,863.
354 Ali M, Ueki T, Tsurumi D, Hirai T, *Langmuir*, **27**, 7902-8, 2011.
355 Boersma A, **US Patent Application Publication US 2010/0148632**, Jun. 17, 2010.
356 Dornau P, Russo R R, Tieger J, **US Patent Application Publication US 2006/0135667**, *Star Brite Distributing, Inc.*, Jun. 22, 2006.
357 Bellino M T, Randolph C M, Srinivasan K R, **US Patent Application Publication US 2006/0275681**, *Lexmark International, Inc.*, Dec. 7, 2006.
358 **US Patent** 6,465,099.
359 **US Patent** 6,419,981.
360 **US Patent** 6,413,633.
361 **US Patent** 6,294,252.
362 **US Patent** 6,261,677.
363 **US Patent** 6,194,071.
364 **US Patent** 6,045,908.
365 **US Patent** 5,976,440.
366 **US Patent** 5,875,788.
367 **US Patent** 5,858,530.
368 **US Patent** 5,776,609.
369 **US Patent** 5,707,737.
370 **US Patent** 5,658,663.
371 **US Patent** 5,614,574.
372 **US Patent** 5,605,757.
373 Lin C-Y, Chapman B R, Cheng C Y, Ferry W M, Kelly M B, Lundmark B R, Li W, *US Patent Application Publication US 2006/0008643*, *ExxonMobil*, Jan. 12, 2006.
374 Phan D V, **US Patent 7,670,678 B2**, *The Procter & Gamble Company*, Mar. 2, 2010.
375 Li W, Lin C-Y, Chapman B R, Kelly M B, **US Patent Application Publication US 2004/0186214**, *ExxonMobil*, Sep. 23, 2004.
376 **US Patent** 5,579,429.
377 Shashoua Y, *Polym. Preprints*, **41**, 2, 2000, p.1796-7.
378 Audic J-L; Poncin-Epaillard F; Reyx D; Brosse J-C, *J. Appl. Polym. Sci.*, **79**, No.8, 22nd Feb.2001, p.1384-93.
379 Uzomah T C; Ugbolue S C O, *J. Mater. Sci.*, **34**, No.16, 15th Aug.1999, p.4057-64.
380 Ming Y; Meier D J, *Polym. Mater. Sci. Eng.*, **76**, 1997, p.25-6.
381 **US Patent** 6,479,193.
382 **US Patent** 6,479,162.

- 383 US Patent 6,476,892.
384 US Patent 6,468,609.
385 US Patent 6,452,264.
386 US Patent 6,432,547.
387 US Patent 6,418,661.
388 US Patent 6,403,276.
389 US Patent 6,403,005.
390 US Patent RE37,699.
391 US Patent 6,383,619.
392 US Patent 6,358,503.
393 US Patent 6,320,042.
394 US Patent 6,316,067.
395 US Patent 6,291,565.
396 US Patent 6,280,835.
397 US Patent 6,270,866.
398 US Patent 6,263,552.
399 US Patent 6,255,388.
400 US Patent 6,248,817.
401 US Patent 6,245,175.
402 US Patent 6,235,374.
403 US Patent 6,214,530.
404 US Patent 6,207,792.
405 US Patent 6,166,117.
406 US Patent 6,133,352.
407 US Patent 6,127,438.
408 US Patent 6,036,913.
409 US Patent 6,008,940.
410 US Patent 5,972,519.
411 US Patent 5,962,053.
412 US Patent 5,929,133.
413 US Patent 5,928,834.
414 US Patent 5,914,194.
415 US Patent 5,914,073.
416 US Patent 5,875,014.
417 US Patent 5,856,468.
418 US Patent 5,843,581.
419 US Patent 5,824,398.
420 US Patent 5,806,834.
421 US Patent 5,759,702.
422 US Patent 5,736,066.
423 US Patent 5,726,229.
424 US Patent 5,705,632.
425 US Patent 5,688,455.
426 US Patent 5,641,562.
427 US Patent 5,626,969.
428 US Patent 5,614,297.
429 US Patent 5,611,985.
430 US Patent 5,591,520.
431 US Patent 5,589,126.
432 US Patent 5,569,482.
433 US Patent 5,514,473.
434 McCarron P A, Woolfson D, Donnelly R F, Andrews G P, Zawislak A, Price J H, *J. Appl. Polym. Sci.*, **91**, 1576-89, 2004.
435 Nielsen S K, **US Patent Application Publication US 2009/0246496**, Oct. 1, 2009.
436 Kubler S, Eberhardt S, Arends P, Siemann U, **US Patent Application Publication US 2010/0316861**, *Lofo High Tech Film GmbH*, Dec. 16, 2010.
437 Percec S, Pollino J M, **US Patent Application Publication US 2011/0147680**, *DuPont*, Jun. 23, 2011.
438 Hamdani M; Thil L; Gans G; Feigenbaum A E, *J. Appl. Polym. Sci.*, **83**, No.5, 31st Jan.2002, p.956-66.
439 Hemmerlin C O; Pham Q T, *Polymer*, **41**, No.12, 2000, p.4401-7.
440 Murphy J, *Plast. Additives Compounding*, **2**, No.2, Feb.2000, p.18-22.

- 441 Risch S J, 1998 Polym. Laminations Coat. Conference. Book 2. Conf. proc., TAPPI, San Francisco, Ca., 30th Aug.-3rd Sept.1998, p.1157-9.
- 442 Shit S C, *Popular Plast. Packaging*, **44**, No.8, Aug.1999, p.49/56.
- 443 Simoneau C; Hannaert P, *Food Additives Contaminants*, **16**, No.25, 1st May 1999, p.197-206.
- 444 Boccacci Mariani M, Chiacchierini E, Gesmundo C, *Food Additives Contaminants*, **16**, No.5, 1999, p.207-213.
- 445 Bichara A; Fugit J L; Taverdet J L, *J. Appl. Polym. Sci.*, **72**, No.1, 4th April 1999, p.49-58.
- 446 Papaspyrides C D; Tingas S G, *Food Additives Contaminants*, **15**, No.6, 1st Aug.1998, p.681-9.
- 447 Hammarling L; Gustavson H; Svensson K; Karlsson S; Oskarsson A, *Food Additives Contaminants*, **15**, No.2, 1998, p.203-8.
- 448 Sidwell J, **Food Contact Polymeric Materials**, *Rapra Technol. Ltd.*, Shawbury, Rapra Technol. Ltd., 1992, pp.112. 12ins. 30/6/97. Rapra Review Rept. No.61, Vol.6, No.1, 1992.
- 449 Hamdani M; Feigenbaum A, *Food Additives Contaminants*, **13**, No.6, Aug/Sept.1996, p.717-30.
- 450 *Eur. Chem. News*, **65**, No.1719, 3rd-9th June 1996, p.37.
- 451 Isley J M; Gott S L, *J. Vinyl Additive Technol.*, **1**, No.4, Dec.1995, p.213-6.
- 452 Fordham P J; Gramshaw J W; Crews H M; Castle L, *Food Additives Contaminants*, **12**, No.5, Sept-Oct.1995, p.651-69.
- 453 Petersen J H; Naamansen E T; Nielsen P A, *Food Additives Contaminants*, **12**, No.2, March/April 1995, p.245-53.
- 454 **US Patent** 6,491,783.
- 455 **US Patent** 6,448,323.
- 456 **US Patent** 6,403,130.
- 457 **US Patent** 6,379,726.
- 458 **US Patent** 6,342,245.
- 459 **US Patent** 6,313,167.
- 460 **US Patent** 6,313,105.
- 461 **US Patent** 6,278,008.
- 462 **US Patent** 6,274,162.
- 463 **US Patent** 6,245,374.
- 464 **US Patent** 6,235,825.
- 465 **US Patent** 6,200,404.
- 466 **US Patent** 6,168,820.
- 467 **US Patent** 6,120,821.
- 468 **US Patent** 6,083,586.
- 469 **US Patent** 6,030,673.
- 470 **US Patent** 5,980,955.
- 471 **US Patent** 5,939,205.
- 472 **US Patent** 5,922,388.
- 473 **US Patent** 5,824,358.
- 474 **US Patent** 5,811,162.
- 475 **US Patent** 5,723,507.
- 476 **US Patent** 5,709,827.
- 477 **US Patent** 5,662,953.
- 478 **US Patent** 5,630,871.
- 479 **US Patent** 5,573,800.
- 480 **US Patent** 5,501,886.
- 481 **US Patent** 5,480,973.
- 482 Guart a, Bono-Blay F, Borrell A, Lacorte S, *Food Addit. Contaminants*, **28**, 5, 676-85, 2011.
- 483 Bueno-Ferrer C, Garrigos M C, Jimenez, A, *Polym. Deg. Stab.*, **95**, 2207-12, 2010.
- 484 Fankhauser-Noti A, Grob K, *Trends Food Sci. Technol.*, **17**, 105-112, 2006.
- 485 Chu H, McMIndes M K, Wu S, **US Patent Application Publication US 2007/0031542**, Feb. 8, 2007.
- 486 Krochta J M, Dangaran K L, Lin S-Y, **US Patent Application Publication US 2005/0191390**, *The Regents of the University of California*, Sep. 1, 2005.
- 487 Bohnert T; Izadi R; Pitman S; Stanhope B, *J. Vinyl Additive Technol.*, **5**, No.3, Sept.1999, p.143-7.
- 488 Colletti T A; Renshaw J T; Schaefer R E, *J. Vinyl Additive Technol.*, **4**, No.4, Dec.1998, p.233-9.
- 489 Bohnert T; Izadi R; Pitman S; Stanhope B, Antec '98. Volume III. Conf. proc., SPE, Atlanta, Ga., 26th-30th April 1998, p.3284-90.
- 490 Colletti T A; Renshaw J T; Schaefer R E, Antec '98. Volume III. Conf. proc., SPE, Atlanta, Ga., 26th-30th April 1998, p.3272-7.
- 491 **US Patent** H2,041.

- 492 US Patent 6,413,618.
493 US Patent 6,146,711.
494 US Patent 6,022,606.
495 US Patent 6,001,925.
496 US Patent 5,955,173.
497 US Patent 5,772,941.
498 US Patent 5,721,302.
499 US Patent 5,679,721.
500 US Patent 5,629,365.
501 US Patent 5,578,363.
502 Mohanty A K, Drzal L T, Rook B P, Misra M, **US Patent 7,354,656**, *Michigan State University*, Apr. 8, 2008.
503 Godwin A D, Naert D, **US Patent 7,629,413**, *ExxonMobil*, Dec. 8, 2009.
504 Horton S D, **US Patent Application Publication US 2011/0123818**, *PolyOne Corporation*, May 26, 2011.
505 Mohanty A K, Drzal L T, Rook B P, Misra, **US Patent 7,354,656**, *Michigan State University*, Apr. 8, 2008.
506 US Patent 5,489,458.
507 US Patent 6,500,873.
508 US Patent 6,478,995.
509 US Patent 6,465,535.
510 US Patent 6,455,610.
511 US Patent 6,455,605.
512 US Patent 6,429,234.
513 US Patent 6,420,015.
514 US Patent 6,414,045.
515 US Patent 6,413,455.
516 US Patent 6,406,648.
517 US Patent 6,386,579.
518 US Patent 6,376,440.
519 US Patent 6,359,021.
520 US Patent 6,350,789.
521 US Patent 6,331,576.
522 US Patent 6,319,441.
523 US Patent 6,294,589.
524 US Patent 6,288,133.
525 US Patent 6,268,046.
526 US Patent 6,262,134.
527 US Patent 6,221,924.
528 US Patent 6,214,894.
529 US Patent 6,190,751.
530 US Patent 6,162,309.
531 US Patent 6,160,028.
532 US Patent 6,140,379.
533 US Patent 6,136,874.
534 US Patent 6,130,268.
535 US Patent 6,103,152.
536 US Patent 6,013,210.
537 US Patent 6,008,262.
538 US Patent 5,990,186.
539 US Patent 5,869,171.
540 US Patent 5,851,461.
541 US Patent 5,817,860.
542 US Patent 5,776,993.
543 US Patent 5,705,536.
544 US Patent 5,633,291.
545 US Patent 5,624,968.
546 US Patent 5,622,662.
547 US Patent 5,576,094.
548 US Patent 5,527,834.
549 Arendt W D, Joshi M V, McConnell W W, Rausch K A, Streeter B E, Strepka A M, **US Patent Application Publication US 2006/0241197**, *Velsicol Chemical Corporation*, Oct. 26, 2006.

- 550 Arendt W D, Joshi, **US Patent Application Publication US 2008/0139680**, *Velsicol Chemical Corporation*, Jun. 12, 2008.
- 551 Park E H, Park B H, Jung Y K, Park Y M, Park S C, **US Patent Application Publication US 2005/0187322**, Aug. 25, 2005.
- 552 Olang F N, O'Leary R J, Korwin Edson M, Quinn R E, **US Patent Application Publication US 2010/0189908**, *Owens Corning*, Jul. 29, 2010.
- 553 **US Patent** 6,477,790.
- 554 **US Patent** 6,461,392.
- 555 **US Patent** 6,432,547.
- 556 **US Patent** 6,391,405.
- 557 **US Patent** 6,348,255.
- 558 **US Patent** 6,324,703.
- 559 **US Patent** 6,280,815.
- 560 **US Patent** 6,277,408.
- 561 **US Patent** 6,235,805.
- 562 **US Patent** 6,228,933.
- 563 **US Patent** 6,219,941.
- 564 **US Patent** 6,180,703.
- 565 **US Patent** 6,166,160.
- 566 **US Patent** 6,139,795.
- 567 **US Patent** 6,136,136.
- 568 **US Patent** 6,041,520.
- 569 **US Patent** 5,985,383.
- 570 **US Patent** 5,922,776.
- 571 **US Patent** 5,872,182.
- 572 **US Patent** 5,829,171.
- 573 **US Patent** 5,756,195.
- 574 Takada K, **US Patent Application Publication US 2006/0048414**, *Okada*, Mar. 9, 2006.
- 575 Baek J K, **US Patent Application Publication US 2005/0274044**, *DC Shoes, Inc.*, Dec. 15, 2005.
- 576 Badding M E, Brown J L, Garner S M, Ketcham T D, Julien D J, **US Patent 7,947,213**, *Corning Incorporated*, May 24, 2011.
- 577 Cho M-d, Sun H-y, Lee M-j, **US Patent Application Publication US 2006/0263659**, Nov. 23, 2006.
- 578 Finnerty C, Cai J, **US Patent Application Publication US 2009/0023050**, Jan. 22, 2009.
- 579 **US Patent** 5,755,045.
- 580 **US Patent** 6,290871.
- 581 **US Patent** 6,232,431.
- 582 **US Patent** 6,210,601.
- 583 **US Patent** 6,155,922.
- 584 **US Patent** 6,011,108.
- 585 **US Patent** 5,700,360.
- 586 **US Patent** 5,487,239.
- 587 **US Patent** 5,171,508.
- 588 **US Patent** 5,061,247.
- 589 **US Patent** 4,870,128.
- 590 **US Patent** 4,861,076.
- 591 Kojima Y, Fujimoto K, Koga a, Senda K, **US Patent 7,099,111**, *NOK Corporation*, Aug. 29, 2006.
- 592 Hasegawa N, Nakagawa Y, **US Patent Application Publication US 2007/0161732**, *Kaneka Corporation*, Jul. 12, 2007.
- 593 Kawakami T, Isama K, Matsuoka A, *J. Environ. Sci. Health Part A*, **46**, 855-64, 2011.
- 594 *Pitture e Vernici*, **70**, No.10, Oct.1994, p.9-20.
- 595 **US Patent** 6,503,965.
- 596 **US Patent** 6,498,203.
- 597 **US Patent** 6,497,481.
- 598 **US Patent** 6,487,774.
- 599 **US Patent** 6,481,843.
- 600 **US Patent** 6,467,899.
- 601 **US Patent** 6,464,766.
- 602 **US Patent** 6,460,957.
- 603 **US Patent** 6,439,710.
- 604 **US Patent** 6,437,023.

- 605 US Patent 6,425,948.
606 US Patent 6,414,051.
607 US Patent 6,395,078.
608 US Patent 6,379,444.
609 US Patent 6,334,890.
610 US Patent 6,319,310.
611 US Patent 6,305,865.
612 US Patent 6,280,028.
613 US Patent 6,261,347.
614 US Patent 6,255,363.
615 US Patent 6,245,136.
616 US Patent 6,245,135.
617 US Patent 6,221,138.
618 US Patent 6,126,731.
619 US Patent 6,117,562.
620 US Patent 6,113,679.
621 US Patent 6,110,264.
622 US Patent 6,103,781.
623 US Patent 6,099,631.
624 US Patent 6,059,871.
625 US Patent 6,042,641.
626 US Patent 6,022,909.
627 US Patent 6,010,564.
628 US Patent 5,981,625.
629 US Patent 5,972,088.
630 US Patent 5,966,150.
631 US Patent 5,958,169.
632 Chen T, Sen R, **US Patent Application Publication US 2006/0038871**, *Hewlett Packard Company*, Feb. 23, 2006.
633 Moss P J, Syed A, Renner T A, **US Patent Application Publication US 2008/0000385**, *Videojet Technologies Inc.*, Jan. 3, 2008.
634 Sugai M, Aoai T, **US Patent Application Publication US 2006/0213391**, *Fuji Photo Film*, Sep.28, 2006.
635 US Patent 5,939,468.
636 US Patent 5,936,027.
637 US Patent 5,919,858.
638 US Patent 5,919,838.
639 US Patent 5,891,228.
640 US Patent 5,880,214.
641 US Patent 5,807,625.
642 Dumitrascu N; Borcia G; Popa G, *J. Appl. Polym. Sci.*, **81**, No.10, 6th Sept.2001, p.2419-25.
643 Lamba N M K; Courtney J M; Gaylor J D S; Lowe G D O, *BioMater.*, **21**, No.1, 2000, p.89-96.
644 Yin H Q; Zhao X B; Courtney J M; Blass C R; West R H; Lowe G D O, *J. Mater. Sci. Mater. Medicine*, **10**, No.9, Sept.1999, p.527-31.
645 Bichara A; Fugit J L; Taverdet J L, *J. Appl. Polym. Sci.*, **72**, No.1, 4th April 1999, p.49-58.
646 *Plast. Technol.*, **45**, No.5, May 1999, p.60-1.
647 Jain K K; Fatma K; Saroop M, *Popular Plast. Packaging*, **43**, No.11, Nov.1998, p.75/82.
648 Lakshmi S; Jayakrishnan A, *Polymer*, **39**, No.1, 1998, p.151-7.
649 Knabe C; Grosse-Siestrup C; Hunder A; Ziemann A, *J. Mater. Sci. Mater. in Medicine*, **8**, No.9, Sept.1997, p.577-82.
650 Luther D W; Linsky L A, *J. Vinyl Additive Technol.*, **2**, No.3, Sept.1996, p.190-2.
651 Lindhout T; Blezer R; Maassen C; Heijnen V; Reutelingsperger C P M, *J. Mater.Sci., Mater. Medicine*, **6**, No.6, June 1995, p.367-72.
652 Kicheva Y I; Kostov V D; Chichovska M, *BioMater.*, **16**, No.7, 1995, p.575-9.
653 US Patent 6,468,258.
654 US Patent 6,458,886.
655 US Patent 6,455,161.
656 US Patent 6,451,912.
657 US Patent 6,443,096.
658 US Patent 6,431,219.
659 US Patent 6,375,977.

- 660 **US Patent** 6,348,049.
661 **US Patent** 6,319,243.
662 **US Patent** 6,273,875.
663 **US Patent** 6,184,285.
664 **US Patent** 6,148,830.
665 **US Patent** 6,099,926.
666 **US Patent** 6,060,138.
667 **US Patent** 5,985,962.
668 **US Patent** 5,968,619.
669 **US Patent** 5,800,412.
670 **US Patent** 5,783,209.
671 **US Patent** 5,772,960.
672 Shuguang Cao, Yanqiao Shi, Guanwen Chen, *Polym. Intl.*, **49**, No.2, Feb.2000, p.209-15.
673 Simmchen J, Ventura R, Segura J, *Transfusion Medicine Rev.*, **26**, 1, 27-37, 2012.
674 Sampson J, de Korte D, *Transfusion Medicine*, **21**, 73-83, 2011.
675 Gourlay T, Shedden L, Horne D, Stefanou D M, *Perfusion* **25**, 1, 31-39, 2010.
676 Dias A M A, Marceneiro S, Braga M E M, Coelho J F J, Ferreira A G M, Simoes P N, Veiga H I M, Tome L C, Maarruch I M, Esperanca M S S, Matias A A, Duarte C M M, Rebelo L P N, de Sousa H C, *Acta Biomater.*, **8**, 1366-79, 2012.
677 Chillini F, Ferri M, Latini G, *Int. J. Pharm.*, **409**, 57-61, 2011.
678 Ahmed S, Mehmood M, Iqbal R, *Radiat. Phys. Chem.*, **79**, 339-42, 2010.
679 Gale D C, Kleine K, Abbate A J, Atladottir S M, Pacetti S D, **US Patent 7,229,471**, *Advanced Cardiovascular Systems Inc.*, Jun. 12, 2007.
680 King R, Hanes M, **US Patent Application Publication US 2009/0171264**, DePuy Products, Jul. 2, 2009.
681 Gale D C, Kleine K, Abbate A J, Atladottir S M, Pacetti S D, **US Patent Application Publication US 2010/0137471**, Jun. 3, 2010.
682 Palasis M, Naimark W, Richard R E, **US Patent Application Publication US 2009/0138076**, *Boston Scientific Scimed, Inc.*, May 28, 2009.
683 Stankus J, Trollsas M, Hossainy S, Pacetti S, Ngo M, **US Patent Application Publication US 2011/0143014**, Jun. 16, 2011.
684 Kawamura N, Sawada H, Kobayashi T, **US Patent Application Publication US 2011/0236440**, Sep. 29, 2011.
685 Yanming Mi; Bakker E, *Analytical Chem.*, **71**, No.23, 1st Dec.1999, p.5279-87.
686 Ye Q; Borbely S; Horvai G, *Analytical Chem.*, **71**, No.19, 1st Oct.1999, p.4313-20.
687 Donempudi S; Yaseen M, *Polym. Eng. Sci.*, **39**, No.3, March 1999, p.399-405.
688 Totu E; Segal E; Covington A K, *J. Thermal Analysis Calorimetry*, **52**, No.2, 1998, p.383-91.
689 Keplinger F J; Jachimowicz A; Kohl F, *Analytical Chem.*, **70**, No.20, 15th Oct.1998, p.4271-9.
690 Perez-Jimenez C; Escriche L; Casabo J, *Analytica Chimica Acta*, **371**, Nos.2-3, 1998, p.155-62.
691 Gibbons W S; Kusy R P, *Polymer*, **39**, No.14, 1998, p.3167-78.
692 Giroud J P, *Geosynthetics Intl.*, **2**, No.6, 1995, p.1099-113.
693 Okada T; Sugihara H; Hiratani K, *Analyst*, **120**, No.9, Sept. 1995, p.2381-6.
694 **US Patent** 6,491,949.
695 **US Patent** 6,444,343.
696 **US Patent** 6,432,571.
697 **US Patent** 6,391,405.
698 **US Patent** 6,391,174.
699 **US Patent** 6,372,379.
700 **US Patent** 6,321,465.
701 **US Patent** 6,224,700.
702 **US Patent** 6,214,185.
703 **US Patent** 6,156,274.
704 **US Patent** 6,139,798.
705 **US Patent** 6,127,026.
706 **US Patent** 6,077,613.
707 **US Patent** 5,958,997.
708 **US Patent** 5,873,915.
709 **US Patent** 5,860,255.
710 Murata H, Naruto H, **US Patent Application Publication US 2010/0285348**, Nov. 11, 2010.
711 Shimizu A, Kondo M, Yamamoto J, **US Patent Application Publication US 2010/0212504**, Aug. 24, 2010.

- 712 Suzuki K, Tada Y, Takahashi T, Hino M, Abe K, Mizuno T, **US Patent Application Publication US 2008/0156722**, Jul. 3, 2008.
- 713 Samanta S, Wiercinski R A, **US Patent Application Publication US 2010/0196648**, *W. R. Grace*, Aug. 5, 2010.
- 714 Sengel-Turk C T, Hascicek C, Gonul N, *AAPS PharmSciTech*, **12**, 4, 1127-35, 2011.
- 715 Boey Y C F, Ma J, Wang Z, **US Patent Application Publication US 2001/0027376**, *Nanyang Technological University*, Feb. 3, 2011.
- 716 Figuly G D, Gommeren H J C, Liu G, **US Patent Application Publication US 2011/0033608**, *DuPont*, Feb. 10, 2011.
- 717 Zhuravleva I I; Laktionov V M, *Intl. Polym. Sci. Technol.*, **26**, No.7, 1999, p.T/50-3.
- 718 Aznar A C; Caprari J J; Meda J F; Slutzky O, *J. Coat. Technol.*, **69**, No.868, May 1997, p.33-8.
- 719 *J. Coat. Technol.*, **68**, No.858, July 1996, p.78-98.
- 720 Athey R D, *Eur. Coat. J.*, No.10, 1996, p.720/30.
- 721 *Chem. Eng. News*, **74**, No.42, 14th Oct.1996, p.50-60.
- 722 Guthrie J T, *Surface Coat. Intl.*, **79**, No.6, June 1996, p.268-73.
- 723 Vecera M, *Pitture Vernici*, **71**, No.11, June 1995, p.14-20.
- 724 Ulyatt J, *Pitture Vernici*, **71**, No.11, June 1995, p.29-33.
- 725 **US Patent** 6,503,629.
- 726 **US Patent** 6,478,861.
- 727 **US Patent** 6,472,114.
- 728 **US Patent** 6,471,843.
- 729 **US Patent** 6,464,823.
- 730 **US Patent** 6,458,848.
- 731 **US Patent** 6,455,598.
- 732 **US Patent** 6,451,141.
- 733 **US Patent** 6,443,202.
- 734 **US Patent** 6,440,332.
- 735 **US Patent** 6,429,244.
- 736 **US Patent** 6,413,642.
- 737 **US Patent** 6,410,635.
- 738 **US Patent** 6,403,826.
- 739 **US Patent** 6,391,961.
- 740 **US Patent** 6,376,067.
- 741 **US Patent** 6,369,134.
- 742 **US Patent** 6,365,271.
- 743 **US Patent** 6,362,252.
- 744 **US Patent** 6,361,826.
- 745 **US Patent** 6,358,567.
- 746 **US Patent** 6,340,519.
- 747 **US Patent** 6,340,503.
- 748 **US Patent** 6,333,378.
- 749 **US Patent** 6,296,730.
- 750 **US Patent** 6,277,903.
- 751 **US Patent** 6,277,160.
- 752 **US Patent** 6,262,149.
- 753 **US Patent** 6,250,512.
- 754 **US Patent** 6,231,789.
- 755 **US Patent** 6,231,650.
- 756 **US Patent** 6,230,452.
- 757 **US Patent** 6,218,448.
- 758 **US Patent** 6,217,432.
- 759 **US Patent** 6,211,260.
- 760 **US Patent** 6,187,042.
- 761 **US Patent** 6,172,132.
- 762 **US Patent** 6,169,141.
- 763 **US Patent** 6,153,709.
- 764 **US Patent** 6,124,401.
- 765 **US Patent** 6,123,987.
- 766 **US Patent** 6,063,855.
- 767 **US Patent** 6,042,638.

- 768 **US Patent** 5,997,894.
769 **US Patent** 5,990,228.
770 **US Patent** 5,981,646.
771 **US Patent** 5,977,228.
772 **US Patent** 5,935,661.
773 **US Patent** 5,928,394.
774 **US Patent** 5,916,669.
775 **US Patent** 5,891,579.
776 **US Patent** 5,885,617.
777 **US Patent** 5,877,231.
778 **US Patent** 5,863,967.
779 **US Patent** 5,830,937.
780 **US Patent** 5,824,373.
781 **US Patent** 5,795,374.
782 **US Patent** 5,789,039.
783 Rodriguez M T, Gracenea J J, Garcia S J, Saura J J Suay J J, *Prog. Org. Coat.*, **50**, 123-31, 2004.
784 Dellinger D A, Helou E, Speer D V, Schwark D W, **US Patent Application Publication US 2010/0203348**, *Perkins Coie LLP*, Aug. 12, 2010.
785 Signorino C A, Smith T L, Levine S, **US Patent Application Publication US 2011/0269850**, Nov. 3, 2011.
786 Mead D H, Rogers D M, **US Patent Application Publication US 2011/0079347**, *PPG Industries Ohio, Inc.*, Apr. 7, 2011.
787 **US Patent** 5,783,303.
788 Pfannschmidt O; Michaeli W, Antec '99. Volume III. Conf. proc., SPE, New York City, 2nd-6th May 1999, p.2985-8.
789 Govender T; Dangor C M, *J. Microencapsulation*, **14**, No.4, July-Aug.1997, p.445-55.
790 Beck M I; Tomka I, *J. Polym. Sci.: Polym. Phys. Ed.*, **35**, No.4, March 1997, p.639-53.
791 Beck M I; Tomka I, *Macromolecules*, **29**, No.27, 30th Dec.1996, p.8759-69.
792 Nimmannit U; Suwanpatra N, *J. Microencapsulation*, **13**, No.6, Nov.-Dec.1996, p.643-9.
793 Palomo M E; Ballesteros M P; Frutos P, *J. Microencapsulation*, **13**, No.3, May-June 1996, p.307-18.
794 Czuba L; Puryear H; Sarkar K, Medical Design Manufacturing, Orlando. Conf. proc., Canon Communications Inc.; Medical Device & Diagnostic Ind. Magazine; SPE, Medical Plast. Div., Orlando, Fl., 20th Sept.1995, p.73-84.
795 **US Patent** 6,500,859.
796 **US Patent** 6,500,462.
797 **US Patent** 6,500,469.
798 **US Patent** 6,500,457.
799 **US Patent** 6,500,431.
800 **US Patent** 6,495,591.
801 **US Patent** 6,495,163.
802 **US Patent** 6,492,428.
803 **US Patent** 6,492,402.
804 **US Patent** 6,489,312.
805 **US Patent** 6,486,174.
806 **US Patent** 6,482,848.
807 **US Patent** 6,479,548.
808 **US Patent** 6,475,493.
809 **US Patent** 6,468,561.
810 **US Patent** 6,465,451.
811 **US Patent** 6,458,818.
812 **US Patent** 6,458,383.
813 **US Patent** 6,455,073.
814 **US Patent** 6,448,323.
815 **US Patent** 6,437,000.
816 **US Patent** 6,436,438.
817 **US Patent** 6,432,448.
818 **US Patent** 6,428,810.
819 **US Patent** 6,423,256.
820 **US Patent** 6,419,956.
821 **US Patent** 6,417,218.
822 **US Patent** 6,410,054.

- 823 **US Patent** 6,395,298.
824 **US Patent** 6,391,342.
825 **US Patent** 6,372,246.
826 **US Patent** 6,368,628.
827 **US Patent** 6,365,184.
828 **US Patent** 6,344,211.
829 **US Patent** 6,342,245.
830 **US Patent** 6,331,316.
831 **US Patent** 6,316,020.
832 **US Patent** 6,309,666.
833 **US Patent** 6,306,435.
834 **US Patent** 6,306,428.
835 **US Patent** 6,284,275.
836 **US Patent** 6,274,173.
837 **US Patent** 6,267,983.
838 **US Patent** 6,267,808.
839 **US Patent** 6,258,799.
840 **US Patent** 6,248,758.
841 **US Patent** 6,235,311.
842 **US Patent** 6,224,911.
843 **US Patent** 6,183,808.
844 **US Patent** 6,162,466.
845 **US Patent** 6,039,976.
846 **US Patent** 6,027,746.
847 **US Patent** 5,998,478.
848 **US Patent** 5,952,005.
849 Repka M A, Shah S, Lu J, Maddineni S, Morott J, Patwardhan K, Mohammed N N, *Expert Opin. Drug Deliv.*, **9**, 1, 105-125, 2012.
850 Takeshita A, Igarashi-Migitaka J, Nishiyama K, Takahashi H, Takeuchi Y, Koibichi N, *Toxicol. Sci.*, **123**, 2, 460-70, 2011.
851 Schilling S U, Lirola H L, Shah N H, Malick W, McGinity J W, *J. Microencapsulation*, **27**, 6, 521-32, 2010.
852 Kotagale N, Maniyar M, Somvanshi S, Umekar M, Patel C J, *Pharm. Dev. Technol.*, **15**, 4, 431-37, 2010.
853 Rujivipat S, Bodmeier R, *Eur. J. Pharm. Biopharm.*, in press 2012.
854 Hanhijarvi K, Majava T, Kassamakov I, Heinamaki J, Aaltonen J, Haapalainen J, Haggstrom E, Yliruusi J, *Eur. J. Pharm. Biopharm.*, **74**, 371-76, 2010.
855 Gal A, Nussinovitch A, *Int. J. Pharm.*, **370**, 103-9, 2009.
856 Chamarthy S P, Pinal R, *Colloids Surfaces A: Physicochem. Eng. Aspects*, **331**, 25-30, 2008.
857 Siepman F, Le Brun V, Siepman J, *J. Controlled Release*, **115**, 298-306, 2006.
858 Verreck G, Decorte A, Li H, Tomasko D, Arien A, Peeters J, Rombaut P, Van den Mooter G, Brewster M E, *J. Supercritical Fluids*, **38**, 383-91, 2006.
859 Zhu J, Luo Y, Ma L, Zhang H, **US Patent Application Publication US 2011/0114019**, *The University of Western Ontario*, May 19, 2011.
860 Manku M, **US Patent Application Publication US 2010/0278879**, *Amarin Pharma, Inc.*, Nov. 4, 2010.
861 Dyar S C, Lodaya M P, Mollan M J, Shah U, Sun H J, Teweldemedhin Z, **US Patent Application Publication US 2011/0144181**, *Warner-Lambert Company LLC*, Jun. 16, 2011.
862 **US Patent** 6,455,238.
863 **US Patent** 6,455,235.
864 **US Patent** 6,423,486.
865 **US Patent** 6,394,650.
866 **US Patent** 6,361,930.
867 **US Patent** 6,303,280.
868 **US Patent** 6,300,045.
869 **US Patent** 6,281,270.
870 **US Patent** 6,214,767.
871 **US Patent** 6,214,530.
872 **US Patent** 6,197,482.
873 **US Patent** 6,069,196.
874 **US Patent** 6,015,656.
875 **US Patent** 5,998,001.
876 Komohara K, Sata H, Suzuki R, **US Patent Application Publication US 2011/0151145**, *Fuji Film*

- Corporation*, Jun. 23, 2011.
- 877 Kawabe S, Saito K, Suzuki T, Nakamura K, Kasahara K, Yamada R, Nakahara I, **US Patent Application Publication US 2010/0236713**, *Konica Minolta Opto, Inc.*, Sep. 23, 2010.
- 878 Germain Y, *Polym. Eng. Sci.*, **38**, No.4, April 1998, p.657-61.
- 879 **US Patent** 6,301,774.
- 880 **US Patent** 6,177,162.
- 881 **US Patent** 6,145,546.
- 882 **US Patent** 5,876,548.
- 882 **US Patent** 5,591,497.
- 884 **US Patent** 5,536,462.
- 885 **US Patent** 5,525,155.
- 886 **US Patent** 5,512,342.
- 887 **US Patent** 5,485,541.
- 888 **US Patent** 5,406,641.
- 889 **US Patent** 5,385,173.
- 890 Doshi S R, **US Patent Application Publication US 2011/0155359**, *DuPont*, Jun. 30, 2011.
- 891 **US Patent** 5,329,973.
- 892 R M; Delgado A H, *Polym. Mater. Sci. Eng.*, **75**, 2, 1996, p.69-70.
- 893 **US Patent** RE37,683.
- 894 **US Patent** 6,306,937.
- 895 **US Patent** 6,300,394.
- 896 **US Patent** 6,297,324.
- 897 **US Patent** 6,291,571.
- 898 **US Patent** 6,120,869.
- 899 **US Patent** 6,087,419.
- 900 **US Patent** 5,929,144.
- 901 **US Patent** 5,733,621.
- 902 **US Patent** 5,687,517.
- 903 **US Patent** 5,686,179.
- 904 **US Patent** 5,594,073.
- 905 **US Patent** 5,523,357.
- 906 **US Patent** 5,467,568.
- 907 **US Patent** 5,455,291.
- 908 **US Patent** 5,421,876.
- 909 **US Patent** 5,253,461.
- 910 **US Patent** 5,216,053.
- 911 **US Patent** 5,130,355.
- 912 **US Patent** 4,977,720.
- 913 **US Patent** 4,851,463.
- 914 **US Patent** 4,812,356.
- 915 **US Patent** RE32,710.
- 916 **US Patent** 4,666,761.
- 917 **US Patent** 4,659,759.
- 918 **US Patent** 4,600,635.
- 919 **US Patent** 4,574,103.
- 920 Griffin E R, Building a better PVC, DuPont Industrial Polymers.
- 921 Palatinol 11P-E. Technical Data Sheet, February 2001, BASF.
- 922 Fensel F A, Smith J D, **US Patent Application Publication US 2010/0236714**, *Garland Industries, Inc.*, Sep. 23, 2010.
- 923 **US Patent** 6,405,775.
- 924 **US Patent** 6,391,945.
- 925 **US Patent** 6,359,045.
- 926 **US Patent** 6,355,728.
- 927 **US Patent** 6,348,539.
- 928 **US Patent** 6,326,433.
- 929 **US Patent** 6,318,430.
- 930 **US Patent** 6,300,449.
- 931 **US Patent** 6,277,904.
- 932 **US Patent** 6,277,902.
- 933 **US Patent** 6,211,271.

- 934 **US Patent** 6,187,125.
935 **US Patent** 6,130,277.
936 **US Patent** 6,119,743.
937 **US Patent** 6,028,144.
938 **US Patent** 5,967,211.
939 **US Patent** 5,939,484.
940 **US Patent** 5,717,038.
941 **US Patent** 5,605,657.
942 **US Patent** 5,386,864.
943 Recker C, Reese T, Schoening, **US Patent Application Publication US 2011/0112213**, *Continental Reifen Deutschland GmbH*, May 12, 2011.
944 De-Riva Perez J, Weber C, Kramer T, Koelle P, **US Patent Application Publication US 2011/0071245**, Mar. 24, 2011.
945 Mueller G, D'Ignoti V L, Thiede W M T, Juris C, Cocconi C, **US Patent Application Publication US 2011/0253277**, Oct. 20, 2011.
946 Kawaguchi K, Morooka N, **US Patent Application Publication US 2011/0028651**, *The Yokohama Rubber Co., Ltd.*, Feb. 3, 2011.
947 Sato M, Kiyohara T, **US Patent Application Publication US 2011/0086943**, Apr. 14, 2011.
948 Maltoni, C, Long term carcinogenicity bioassays of polyvinylchloride (PVC) administered by ingestion (gavage) on Sprague-Dawley Rats", *Stampa su Acta Oncologica* 1989/4.
949 NTP (National Toxicology Program). 1982. Carcinogenesis bioassay of di-(2-ethylhexyl) phthalate (CAS No. 117-81-7) in F344 rats and B6C3F₁ mice (feed study). NTP Tech. Rep. Ser. TR No. 217, 1982.
950 Some industrial Chemicals, IARC monographs on the Evaluation of Carcinogenic risks to humans, Vol 77, February 2000, p 15-22.
951 Wickson E J, **Handbook of PVC Formulating**, *John Wiley and Sons*, New York, 1993, p 849.
952 Phthalate migration from soft PVC toys and children care articles, Opinion expressed at CSTEE 3rd plenary meeting Brussels, 24th April 1998.
953 Kopp C E, Juberg D R, A Scientific Evaluation of Health Effects of Two Plasticizers used in Medical Devices and Toys: A Report from the American Council on Science and Health, June 1999.
954 Opinion on the toxicological characteristics and risks of certain citrates and adipates used as a substitute for phthalates as plasticizers in certain soft PVC products, opinion adopted at the 11th CSTE plenary meeting on the 28th of September 1999.
955 Opinion on TNO, LGC and U.S. CPSC reports on Phthalate migration test validation adopted at the 11th CSTE plenary meeting on the 28th of September 1999.
956 Official Journal of the European Communities, L 315/46, 9.12.1999.
957 The availability of substitutes for soft PVC containing phthalates in certain toys and children care articles. Final report prepared for the European Commission, Directorate-General Enterprise by Risk & Policy Analyst Limited, U.K., July 2000.
958 USEPA HPV Challenge program Submission. Submitted by Velsicol Chemical Corporation, November 2001.
959 Environmental and Health Assessment of Alternatives to Phthalates and to Flexible PVC, Environmental project N° 590 2001.
960 **US Patent** 6,431,219.
961 **US Patent** 6,378,562.
962 **US Patent** 6,321,795.
963 **US Patent** 6,187,400.
964 **US Patent** 6,060,138.
965 **US Patent** 6,050,980.
966 **US Patent** 5,968,619.
967 **US Patent** 5,941,286.
968 **US Patent** 5,928,216.
969 **US Patent** 5,721,024.
970 Mertz W J, Gates J A, **US Patent 7,211,140**, *Cognis Corporation*, May 1, 2007.
971 Siddhamalli S, Liu Z, Simon M W, Golub C S, Sardinha H, Garver W E, Colton M F, Wells R L, Wells R L, Stadt G L, Tzivanis M J, Risen W, Klettlinger N, **US Patent Application Publication US 2011/0241262**, *Saint-Gobain*, Oct. 6, 2011.
972 Adams R C; Petkus S L, Antec 2000. Conference proceedings, Orlando, Fl., 7th-11th May, 2000, paper 647.
973 Griffin E R, *J. Vinyl Additive Technol.*, **6**, No.4, Dec.2000, p.187-91.
974 Brebu M; Vasile C; Antonie S R; Chiriac M; Precup M; Yang J; Roy C, *Polym. Deg. Stab.*, **67**, No.2, Feb.2000, p.209-21.

- 975 Jakubowicz I; Yarahmadi N; Gevert T, *Polym. Deg. Stab.*, **66**, No.3, 1999, p.415-21.
976 **US Patent** 6,493,491.
977 **US Patent** 6,479,607.
978 **US Patent** 6,410,893.
979 **US Patent** 6,395,975.
980 **US Patent** 6,374,023.
981 **US Patent** 6,369,264.
982 **US Patent** 6,342,679.
983 **US Patent** 6,255,374.
984 **US Patent** 6,245,175.
985 **US Patent** 6,215,931.
986 **US Patent** 6,214,910.
987 **US Patent** 6,191,074.
988 **US Patent** 6,171,669.
989 **US Patent** 6,162,540.
990 **US Patent** 6,114,425.
991 **US Patent** 6,051,315.
992 **US Patent** 6,043,312.
993 **US Patent** 5,963,701.
994 **US Patent** 5,912,436.
995 **US Patent** 5,886,072.
996 **US Patent** 5,817,981.
997 **US Patent** 5,462,803.
998 **US Patent** 5,444,809.
999 Emanuelsson V, Simonson M, Gevert T, *Fire Mater.*, **31**, 311-26, 2007.
1000 Benes M, Placek V, Matuschek G, Kettrup A, Gyoryova K, Balek V, *J. Appl. Polym. Sci.*, **99**, 788-95, 2006.
1001 Benes M, Placek V, Matuschek G, Kettrup A, Gyoryova K, Emmerich W D, Balek V, *J. Therm. Anal. Calorimetry*, **82**, 761-68, 2005.
1002 Ekelund M, Edin H, Gedde U W, *Polym. Deg. Stab.*, **92**, 617-29, 2007.