PERP Program – Trends in Plasticizers
New Report Alert

April 2007

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a report, ***Trends in Plasticizers (05/06S8)***. To view the table of contents or order this report, please click on this link: http://www.chemsystems.com/reports/index.cfm?catID=2

INTRODUCTION

In its broadest definition, a plasticizer is a material that when added to another yields a mixture which is easier to handle or has greater utility. Using water to soften clay or oil to plasticize pitch for waterproofing boats are both examples of early plasticized systems.

The use of plasticizers to modify polymers began in the 1800s, when the Hyatt Brothers added camphor to nitrocellulose to increase the latter's moldability and reduce brittleness. The use of plasticizers in PVC was invented in the 1920s; the first patent on octyl alcohol ester (DOP) as a plasticizer was issued in 1933. DOP was patented for use in PVC in 1943 by B. F. Goodrich.

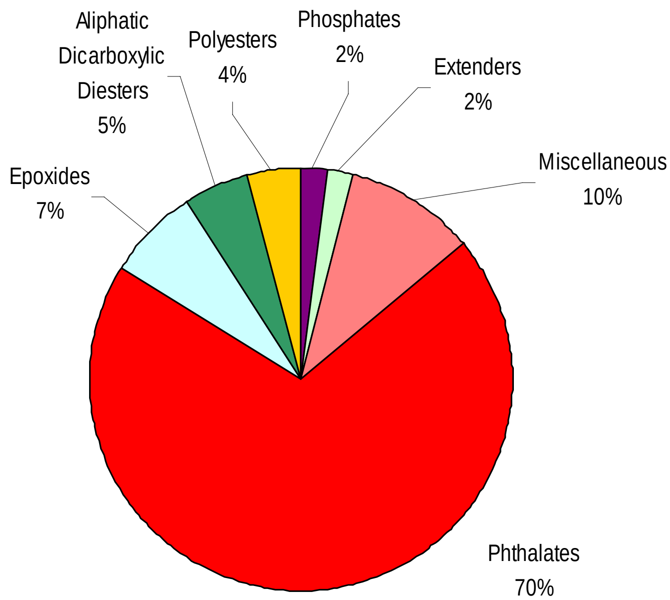
There have been over 500 plasticizers identified, though only between 50 and 100 are used for commercial purposes. About 80-90 percent of all plasticizers are used in PVC. Other end-uses for plasticizers include synthetic rubbers, cellulosics, and acrylics. However, since the bulk of plasticizers are used in PVC, this report will focus on commonly used plasticizers for this polymer, especially the phthalate esters, which account for the majority of plasticizers used in PVC.

Plasticizer performance is best when the molecules contain both polar and non-polar groups. The polar groups help the plasticizer be retained in the system, while the non-polar groups attenuate the attractive forces between the polymer chains to give flexibility. It should be noted that the plasticizer is an integral part of the final product so as to provide long-lived benefits.

Smaller, polar materials are effective in increasing processability as well, although volitization of the plasticizer is an issue. Conversely, polymeric plasticizers are retained better and provide better performance at extremes in temperature, but provide little benefit in processability.

Many different materials are used as plasticizers in PVC. The most commonly used materials are phthalate esters. These colorless, odorless liquids are produced by a simple chemical reaction between an alcohol and phthalic anhydride. An approximate breakdown (for North America) in the kinds of plasticizers used in PVC is shown in Figure 1.

Figure 1 Types of PVC Plasticizers
(North America break-down)



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Phthalates

Produced by the reaction of a suitable alcohol with phthalic anhydride or terephthalic acid, phthalate ester plasticizers are the most extensively used plasticizers in the world. While methanol and up to C_{17} alcohols are utilized to manufacture phthalate ester plasticizers, C_4-C_{10} alcohols are the ones typically used in plasticizers. Linear alcohols can also be used to produce plasticizers, although their use is increasingly out of favor due to the high cost of ethylene (a raw material for these products) as compared to the raw materials for the C_9-C_{10} plasticizers.

Di-2-ethylhexyl phthalate (DEHP; also called di-octylphthalate or DOP) is the phthalate ester produced from the reaction of 2-ethyl hexanol alcohol (derived from propylene) and phthalic anhydride. Even though its health effects have been questioned, it is still widely used as a plasticizer due to its plasticizing performance and low cost.

Increasingly, and especially in commodity all-purpose applications, the C_9 (diisononylphthalate (DINP)) and C_{10} (diisodecylphthalate (DIDP)) iso-phthalate plasticizers are competing with DEHP. It is generally accepted that the C_9 and C_{10} phthalates provide modest cost/benefit performance advantages over DEHP.

Commodity phthalates are used in many applications such as flooring, wall coverings, vinyl skins, sheaths for electric cables, coated fabrics, and shoes. The linear phthalates have lower volatility when compared to the branched phthalates with the same molecular weight. They impart better cold temperature flexibility and resistance to photo-degradation. Consequently, they are used in PVC roofing, anti-fogging synthetic leather for car interiors, and certain automotive electrical cables.

Many other "specialty" phthalates are produced, though volumes are much smaller than DEHP, DINP, or DIDP. Specialty phthalates esters produced from low carbon number alcohols provide rapid fusion. Other specialty phthalates include benzylbutyl phthalate, diisoundecyl phthalate (which possess a low volatility), and semi-linear and linear phthalates (used in applications where plasticizers of low viscosity are needed).

ENVIRONMENTAL ISSUES

Phthalates were first produced in the 1920s, though they found limited commercial use. However, since the 1950s, large quantities of phthalates have been consumed to plasticize PVC. Plasticized PVC is used in applications such as medical tubing, blood bags, footwear, stationery goods, flooring and wall-coverings, electrical cable insulation, clothing and toys. In addition, phthalates are used in other non-PVC applications such as rubber products, paints, printing inks, adhesives, lubricant and some cosmetic products. The most commonly used phthalates are di-2-ethyl hexyl phthalate (DEHP also called dioctyl phthalate (DOP)), diisodecyl phthalate (DIDP, DEHP, diisononyl phthalate (DINP) and dibutyl phthalate (DBP). Other phthalates such as benzyl butyl phthalate (BBP) are used in the manufacture of PVC foam used primary for flooring applications. Of all the phthalates, DEHP is the most widely used, accounting for more that 50 percent of all phthalates used in PVC globally.

Since the early 1980s, there have been concerns regarding the use phthalates and their effects on human health and the environment. The first indication that phthalates could cause an increased incidence of liver tumor in rats and mice was in 1980 after the NTP/NCI Bioassay Program in the U.S. started studying the effect of feeding DEHP to mice. By the late 1980s, there was controversy surrounding the use of plasticized PVC cling film in food packaging applications. There was concern that material from plasticized PVC used in cling film could leach into food and cause harm. However, the plasticizers used in cling film were not phthalates, and cling film was proven safe to use.

By the 1990s, several other issues regarding the use of phthalates were raised. There was concern about their effects on the environment, human reproductive system and function of hormones in the human body. These concerns were based on research performed in the late 1990s on animals (rats), even though results obtained were not relevant to humans. Another major concern surrounding phthalates was their exposure to children via breast milk, toys and medical equipment. A study in Norway showed that bronchial obstruction in children was directly related to the amount of plasticizer-emitting material present in the house. In 1998, toy companies came under attack from activist groups such as Green Peace, who lobbied against PVC use in children products. Consequently, Mattel and First Year stopped using phthalates in their toys by 1999.

As a result of these concerns, the European Commission in 1999 temporarily banned the use of six phthalates in toys which were used in oral applications designed for children under three years old (the concentration of six phthalates (DINP, DBP, DIDP, DNOP, DEHP and BBP) should not be more than 0.1 percent in products intended to be place in the mouth of children under three years old). This temporary ban would subsequently be renewed 23-24 times until a permanent ban was adapted in 2005. This was due to the concerns of over exposure of children to these additives at a critical stage of development. This step was also consistent with previous actions taken by other European governments.

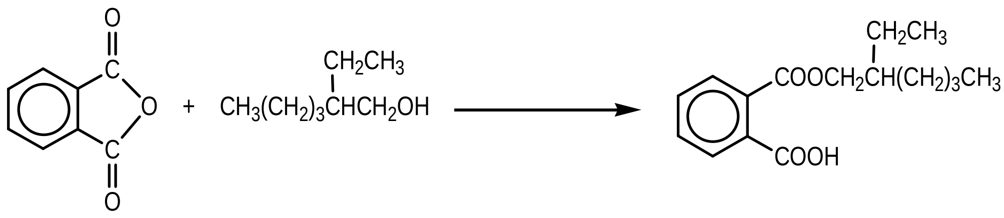
The ongoing debate over phthalates use, especially in Europe, has led to a decrease in the demand for phthalates in the European market for the most common phthalate (i.e., DEHP). Indeed, demand for DEHP started decreasing in 1999. Following declining demand, BASF ceased production of DEHP in October of 2004. Additionally in 2004, a Swedish Danish research group found strong links between allergies and DEHP and BBP. In the same year, a research group from Washington University found no adverse effects in adolescents who were exposed to phthalates during development. However, in early 2005, there was another study showing that phthalates mimicked female hormones, resulting in feminization of boys.

In July 2005, the EU permanently banned the use of DEHP, DBP and BBP in all children's articles. Additionally, the EU banned the use of DINP, DIDP, and DNOP in children's articles which can be put in the mouth. This ban became effective on January 16, 2007. The restriction on the use of phthalates in Europe has pushed other regions to consider reducing the use of these plasticizers even though studies showed that phthalates pose little or no health risks to humans or the environment. Currently, there is a ban on phthalates in San Francisco (U.S.) that is being contested by the American Chemistry Council (the ban was to take effect January 1, 2007, but is delayed because of a law suit). Taiwan took a similar approach and banned the use of two phthalate plasticizers shortly after the ban in Europe. Canada has also put phthalates on its high priority list of chemicals, which should be evaluated similarly to the European Union's Registration, Evaluation and Authorization of Chemicals (REACH) initiative. Large cosmetic companies in the U.S., such as L'Oreal and Revlon, have taken the initiative of banning the use of DBP in their cosmetic products.

CHEMISTRY

A phthalate plasticizer of industrial importance is di-2-ethylhexyl phthalate (DEHP also called dioctyl phthalate or DOP), which is synthesized from phthalic anhydride (PAN) and 2-ethylhexanol (2-EH) according to the following consecutive and/or concurrent equations:

Monoester-Acid Formation



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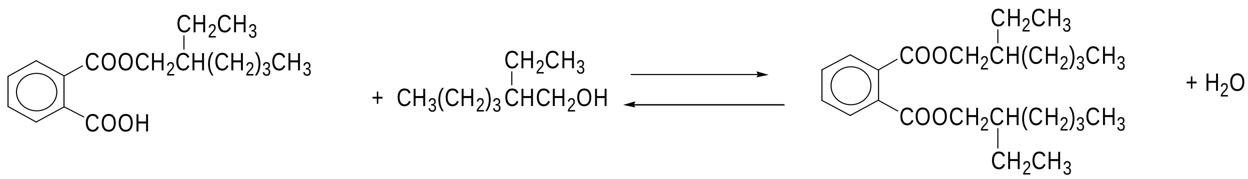
Diester Formation



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Monoester-acid (i.e., 2-ethylhexyl acid phthalate) formation proceeds in the liquid phase, preferably at 110-130°C. Reaction times are about 15 to 30 minutes for complete conversion to the corresponding monoester-acid. The monoester-acid reaction alone is irreversible and can generally be performed without a reaction catalyst. Phthalic anhydride conversion and monoester-acid selectively are virtually quantitative.

Diester formation also proceeds in the liquid phase, preferably at 150-200°C. The equilibrium-controlled diester reaction is generally acid-or base-catalyzed. Amphoteric catalysts function just as well. Homogeneous acid catalysts include sulfuric acid, p-toluenesulfonic acid and hydrochloric acid. Heterogeneous acid catalysts include Lewis acids (e.g. titanium dioxide) and polystyrenesulfonic acid ion-exchange resins in the hydrogen form. Titanium dichloride diacetate is also mentioned. The preferred homogeneous acid catalyst had been p-toluenesulfonic acid. Its lesser oxidizing action (as compared to sulfuric acid) inhibits both alcohol dehydration and color body formation via oxidation of carbonyls (aldehydes) that can be present in the feed oxo alcohol. More recently, organo-titanates and organo-tin compounds have become widely used esterification catalysts. Reaction equilibrium is forced to the right by using excess 2-ethylhexanol to azeotropically remove the water formed and/or by adding entrainers (e.g., toluene or benzene) to azeotrope the byproduct water.

ECONOMICS

Cost of production economics for the following raw materials and plasticizers are presented in the report:

- Phthalic Anydride via Lurgi-BASF Process
- 2-Ethylhexanol via Davy/Dow LP Oxo Selector process
- Mixed Octenes via Axens Dimersol process
- Isononanol via Johnson Matthey unmodified rhodium oxo process
- DOP via batch process
- DOP via continuous process
- INP via batch process
- DINP via continuous process

COMMERCIAL ANALYSIS

This section of the report provides a regional market overview for dioctyl phthalate (DOP) and diisononyl phthalate (DINP) for North America, Western Europe, Japan, South Korea, and China, as well as a global total. The forecast timeframe is to 2011.

China is not only the largest DOP consuming region, it is also among the fastest growing, with growth projected at 2.1 percent per year for the 2006-2011 period. Environmental issues are projected to cause DOP demand to remain almost flat in North America, while decreasing DOP demand in Western Europe and Japan.

Japan, South Korea, and China constituted about 31 percent of the global DINP demand in 2005, and are anticipated to grow to 42 percent of global demand by 2011.

Regional distribution of plasticizer capacity, for the major producers, is provided in the report. The plants are categorized as either DOP only plants for Multipurpose. The term “Multipurpose” refers to capacity that is used to produce a range of plasticizer that include DOP, DINP and others.

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