PERP Program

Developments in Non-Phthalate Plasticizers

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.

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 a plasticizer is an integral part of the final product and provides 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.

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.

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) of the kinds of plasticizers used in PVC is shown in Figure 1.

Phthalate esters, also known as *ortho*-phthalate esters, are one of the three isomeric forms of benzenedicarboxylic acid esters. The other isomeric forms are *meta*-phthalates (or isophthalates) and *para*-phthalates (or terephthalates). It is important to mention that the current environmental and health issues being attributed to plasticizers involve only *ortho*-phthalate esters.

In this report, the word "phthalate" will be use to refer to *ortho*-phthalate esters. While "non-phthalate" will refer to other types of plasticizers such as adipates, citrates, trimellitates, and terephthalates.

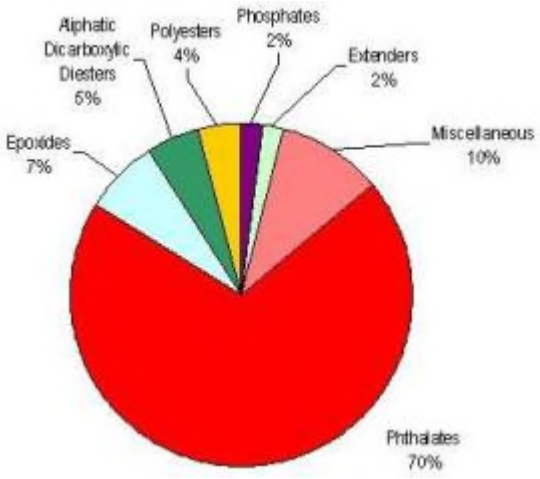


Figure. 1

Types of PVC Plasticizers *(North American break-down)*

Health and Safety Concerns

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 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. In October 2007, California State passed a law (which became effective January 1, 2008) prohibiting the manufacture, sale, and distribution of child care products that contain DEHP, DBP, BBP, DINP, DIDP, and DnOP in concentrations higher than 0.1 percent. Currently, there is pending an United States Senate amendment to ban phthalates from products directed toward children. The United States Chamber of Commerce believes there is no scientific evidence to back up such amendment. 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 United States such as L'Oreal and Revlon, have taken the initiative of banning the use of DBP in their cosmetic products. Toys 'R'Us, a United States' toy retailer, plans to ban phthalates in its juvenile toys by the end of 2008.

Non-Phthalate Plasticizers

The on going scrutiny on phthalates has caused plasticizers producers to concentrate in the research and development of alternative and apparently safer plasticizers.

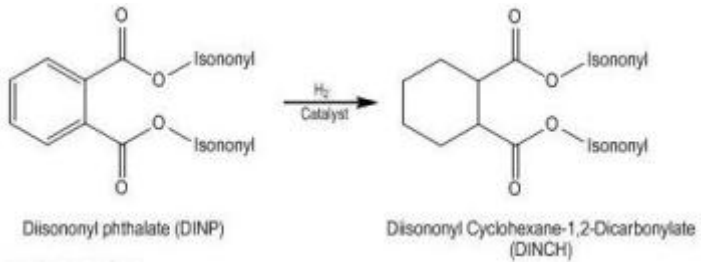
In 2002, BASF introduced an alternative plasticizer for use in PVC applications. Di-isononyl-cyclohexane dicarboxylate (DINCH), marketed under the Hexamoll name, was developed for use in sensitive applications where exposure to toxicological and exposure issues were of great concern such as the manufacturing of toys, medical devices, and food packaging. According to BASF, extensive studies have shown that DINCH possesses no environmental and reproductive hazards as well as no peroxisome proliferation. In October 2006, Hexamoll DINCH received an approval from the European Food Safety Authority (EFSA) making DINCH safe to use in food contact applications such as cling film, tubes, or sealants. Hexamoll DINCH now has German, European, and Japanese Food Contact approvals with a U.S. FDA approval in progress.

Citrates (or citric acid esters), commercialized for more than 35 years, are also use in sensitivity applications since they show benign toxicology. Citrates have been approved to use in applications such as pharmaceutical tablet coatings, medical devices, food packaging (i.e., vinyl film wraps), and cosmetic formulations (i.e., shampoo, deodorants, and fragrances). The main component of citrates is citric acid which is used as a flavoring agent in sports drinks, soft drinks, breakfast juices, and candy bars. In 2004, the European Union Scientific Toxic Committee approved the use of acetyl tributyl citrate (ATBC) for the use in soft PVC toys. According to the panel, ATBC did not possess a safety concern when young children placed PVC contained toys in their mouths.

DINCH and Citrates are not the only non-phthalate plasticizers that have been scrutinized for environmental and health effects. In 2001, the Danish Environmental Protection Agency (DEPA), with the help of COWI Consulting Engineers and Planners, conducted a study that involved the use, exposure, and possible health and environmental effects of 11 substances which include several alternative plasticizers. According to results from the study, the non-phthalate plasticizers are safe to use. The rest of the substances couldn't be assessed for their environmental and health effects since the information on them was limited (i.e., carcinogenicity and acute toxicity). Few of the non-phthalate plasticizers can affect humans which can occur on a working environment such as production of floor and wall covering. However, none of the non-phthalates studied are believe to causes serious damage on organs, genetic material or fetus.

BASF's Hexamoll® DINCH

BASF markets a cycloaliphatic plasticizer under the name Hexamoll DINCH (Di- Iso Nonyl-Cyclo Hexane dicarboxylate). Hexamoll DINCH is the 1,2-cyclohexanedicarboxylic acid diisonyl ester produced by the hydrogenation of the aromatic ring in diisononyl phthalate (DINP), in the presence of a noble catalyst, per the following reaction:



Diisononyl phthalate (DINP) — Diisononyl Cyclohexane-1,2-Dicarbonylate (DINCH)

+ Click image to enlarge

According to BASF, Hexamoll DINCH is a colorless, clear and practically anhydrous liquid with a hardly noticeable odor. It is soluble in the usual organic solvents and is miscible and compatible with all of the monomeric plasticizers commonly used in PVC. Hexamoll DINCH is almost insoluble in water.

BASF claims that, compared to DOP and DINP, Hexamoll DINCH offers improved low temperature performance and that in plastisol applications it offers lower initial viscosity and better viscosity stability.

BASF states that Hexamoll DINCH does not possess environmental hazards, peroxisome proliferation, nor reproductive hazards making it useful in sensitive applications. BASF recommends the use of Hexamoll DINCH in applications that are particularly sensitive based on exposure and toxicological issues such as medical devices (i.e., blood tubes or packaging for nutrient solutions), toys (including those for children under three years of age), and food packaging (as well as artificial wine corks). BASF adds that Hexamoll DINCH can be also be use in sport and leisure products (i.e., gymnastic balls, exercise mats and cushions, and shoes), coating and printing inks, dispersions, textile coatings, and cosmetic applications.

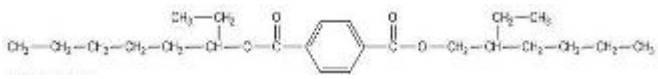
According to BASF, Hexamoll DINCH is suitable for use with PVC and other polar polymers. It is compatible with all of the monomeric plasticizers commonly used in PVC. In most cases, only minor formulation and processing parameter adjustments are required to process flexible PVC compounds.

Terephthalate-Based – Eastman 168

Terephthalates refer to *para*-phthalates (one of the isomeric forms of benzenedicarboxylic acid esters). Thus none of the environmental and health issues associated with plasticizers involve terephthalate esters.

Terephthalates are esters of terephthalic acid. Terephthalate plasticizers include 1,4-benzenedicarboxylic acid sometimes referred as di(2-ethylhexyl) terephthalate (DEHTP) or dioctyl terephthalate (DOTP). Dioctyl terephthalate have similar manufacturing costs as, the other isomeric structure of benzenedicarboxylic acid, dioctyl phthalate (DOP).

Eastman Chemical Company markets a terephthalate plasticizer under the name Eastman 168. Eastman 168 is a 1,4-benzenedicarboxylic acid, bis (2-ethylhexyl) ester that has the following chemical structure:



+ Click image to enlarge

Eastman states that its Eastman 168 plasticizer offers good performance properties, excellent low temperature flexibility, resistance to extraction by soapy water, and excellent non-migration properties. Additionally, Eastman 168 has good lacquer mar resistance where marring of nitrocellulose lacquer by plasticized PVC is common in various applications. In plastisols, Eastman 168 results in low initial viscosity and excellent viscosity stability. It also enables superb processabilty, allowing molders to run at profitable production speeds and faster cycle times, and provides uniform wall thicknesses. According to Eastman, reformulation is unnecessary with Eastman 168 plasticizer, reducing the risk of formulation errors that could result in costly recalls or consumer complaints.

Eastman claims that its Eastman 168 plasticizer can be used in bottle caps and closures, sheet vinyl flooring, flexible film, traffic cones, electric connectors, and other vinyl products

(i.e., vinyl gloves and water stops). Eastman adds that Eastman 168, has a very clean toxicological profile and is neither an estrogen mimicker, carcinogen, nor anti-androgen (i.e., "endocrine disrupter). Therefore, Eastman 168 can be an alternative plasticizer for use in mouthable toys for children under the age of three.

Cost of Production Estimates

Several cases have been considered for the production of plasticizers under a consistent United States Gulf Coast first quarter 2008 price scenario. Furthermore, production cost estimates have been generated for the production of raw materials used in the production of the plasticizers. The plasticizers cost of production estimates were derived utilizing the cost of production plus ROCE values obtained from the respective raw materials cost of production estimates.

The selected cases are:

- Epoxidized Soybean Oil, ESO (USGC, Batch Process)
- Polymeric Ester of Molecular Weight 2,000 (USGC, Batch Process)
- Dioctyl Phthalate, DOP (USGC, Batch Process)
- Eastman 168 (USGC, Batch Process)
- Hexamoll ® DINCH (USGC, Continuous Process)
- Dioctyl Adipate, DOA (USGC, Continuous Process)
- Trioctyl Trimellitate, TOTM (USGC, Continuous Process)

Market Analysis

In addition to the technology and cost assessment, this report also presents market forecasts for PVC, dioctyl phthalate (DOP) and diisononyl phthalate (DINP) as well.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com