DICYCLOPENTADIENE PRODUCTS

A Guide to Product Handling and Use
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1. Introduction

The purpose of this brochure is to review environmental, health and safety aspects for dicyclopentadiene (DCPD), i.e. how to handle DCPD products from Dow according to current industry standards and guidelines.

The Dow Chemical Company (Dow) encourages customers and potential users of their products to review their applications from the standpoint of physical hazards, human health and environmental impact. To help ensure that DCPD products from Dow are not used in ways for which they are not intended or tested, Dow will assist customers in dealing with ecological and product safety considerations.

Product literature, including Material Safety Data Sheets, should be consulted prior to the use of DCPD products from Dow. Dow's commitment to the Responsible Care® initiative of the American Chemistry Council represents Dow's efforts to assist customers in developing sound product stewardship practices to better safeguard workers, operations- and the environment.

1.1 Product Characteristics

Dicyclopentadiene (DCPD), also known as 3a,4,7,7a-tetrahydro-4,7-methano-1H-indene, (endo) or (exo) tricycle[5.2.1.0 (2,6)]deca-3,8-diene or cyclopentadiene dimer is a white crystalline solid at room temperature with a distinctive odor. The Chemical Abstract Service Registry Number (CASRN) is 77-73-6.

It is formed by Diels Alder reaction from two cyclopentadiene molecules and exists in two stereo-isomers: endo-DCPD and exo-DCPD (see Figure 1). Although the exo form of the molecule is thermodynamically more stable, commercial DCPD products contain mostly the endo molecule as it forms much faster than the exo form. Typically > 90% of the DCPD molecules present in commercial grades of DCPD are in the endo form.

Figure 1: Stereo Isomers of DCPD
The Cyclopentadiene (CPD) molecules, from which DCPD products are made, originate from high temperature cracking of petroleum fractions in an ethylene manufacturing process.

DCPD products from Dow can best be characterized as highly reactive intermediates used for a wide range of resins, i.e. aromatic hydrocarbons, unsaturated polyesters, phenolics and epoxies.

Because DCPD concentrates are of variable degrees of purity, their application specifications define not only typical or primary constituents, but also properties that affect finished product performance, such as color or aromatic content for compliance with occupational hygiene requirements.

Codimers, which form a considerable fraction of the "impurities" in the lower purity products, however, do not reduce the performance of the commercial DCPD product. For example: even with 20% codimers, 99% hydrocarbon reaction efficiency is achieved in the production of unsaturated polyester resins.

Dow produces and sells DCPD commercially in three grades: DCPD Resin Grade, DCPD UPR grade and DCPD High Purity. The main constituents of these products are DCPD and CPD codimers, which are Diels Alder adducts of CPD and C4-C6 diolefins. The DCPD products are available in tank truck, railcar or barge quantities. Smaller volumes, up to one metric ton, can be provided on request for experimental and developmental purposes.

1.2 Manufacturing

DCPD Resin Grade and DCPD UPR Grade from Dow are produced by fractionating the C6-C12 products produced in the process of ethylene manufacturing (via thermal cracking of petroleum fractions). The C9-C10 fraction formally contains all kinds of Diels Alder adducts because the various C5 di-olefin molecules form dimers during the process steps of the ethylene manufacturing process. Most predominantly, DCPD molecules are formed and the product is further purified by (vacuum) distillation.

DCPD High Purity from Dow is produced by on-purpose reaction of CPD in a C5 mixture. The reactor product, containing both an unreacted C5 fraction and a C10 fraction, is split by distillation and further purified to produce DCPD High Purity. Because of the controlled way of forming the Diels Alder adducts in the reactor the composition of this product is more defined and can meet higher purity. The DCPD content in DCPD High Purity is the optimum for easy handling / storage and processing economy.

1.3 DCPD (and CPD) Chemistry.

In the presence of a strong acid catalyst, double bond addition products are formed from DCPD and alcohols or carboxylic acids. Reactions with sufficiently strong acids, like maleic acid, are auto-catalytic. A strong acid boost (e.g. with borontrifluoride) is required if an addition is required on the cyclopentenyl ring.
With aqueous sulphuric acid as a catalyst, a secondary alcohol is obtained via hydration, the simplest functionalization of DCPD to suit both the production of resin and derivatives. DCPD can also react with the unsaturated centers in alkyd resin feed such as animal and vegetable oils.

CPD contains two conjugated double bonds and an active methylene group. The bonds allow addition at the 1,4 position with an ethylenic group of another substance, e.g. a dienophile such as maleic anhydride can be reacted to form a bicyclo [2,2,1] heptene derivative (in principle both isomers, endo and exo).

The methylene group is extremely reactive and condenses with aldehydes and ketones to form fulvene derivatives which are strongly coloured and easily form resins. Undesirable products are formed in contact with oxygen, i.e. brown gum and peroxide.

As illustrated in Figure 2, CPD monomer dimerises at room temperature and the rate of dimerisation increases rapidly at higher temperature: 2.5 mole % per hour at 20°C and 15% at 40°C. Such reactions cannot be inhibited with chemicals such as 4-tert-butylcatechol (TBC) and therefore temperature control during storage and/or transport is the only way to limit reaction heat (75 kJ/mole CPD) and consequent product loss.

Above 100°C, the formation of polymer, mainly trimer, tetramer and pentamer, is significant as the result of consecutive Diels-Alder additions of cyclopentadiene, via its dimer.

DCPD is in equilibrium with its monomer CPD. In Figure 3 an example is given of the equilibrium function. It is based on observations during laboratory scale preparation of unsaturated polyester resin and illustrates that the monomerization of DCPD becomes exponential above 140°C and is around 36% per hour at its boiling point, 170°C.
Temperature programming in resin preparation is therefore an important reaction variable that determines how DCPD is included in the structure, either as CPD-adduct or as C10 molecule, and a key parameter in influencing resin properties.

### 1.4 Quality

The current specification for **DCPD Resin Grade** from Dow is based on its application in unsaturated polyester resin manufacture, but also includes parameters which are essential in other uses such as hydrocarbon resins production.

**DCPD UPR Grade** from Dow was developed to meet the specific needs for manufacturing unsaturated polyester resin. Compared to **DCPD Resin Grade**, **DCPD UPR Grade** contains no TriCycloPentaDiene (TCPD), the Diels Alder adduct of DCPD and CPD, and a limited amount of Me-DCPD isomers, the Diels Alder adducts of CPD and methyl-CPD.

Although it is technically possible to produce **DCPD High Purity** from Dow with over 94% DCPD content, Dow limits this for two reasons:

1. customer requirements for resin preparation.
2. avoiding partial crystallization of DCPD and thus enabling easy handling and storage at all ambient temperatures. Figure 4 illustrates how the freezing point changes when the DCPD content is varied.
The analytical methods in Table 1 are used by Dow to check the specification requirements of these DCPD products. It is recommended that customers refer to these analytical methods for quality considerations.

<table>
<thead>
<tr>
<th>Test Item</th>
<th>Method</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity @ 15.56 degC</td>
<td>ASTM D4052</td>
<td></td>
</tr>
<tr>
<td>Available CPD</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Flashpoint</td>
<td>ASTM D93</td>
<td>deg.C</td>
</tr>
<tr>
<td>Sulphur</td>
<td>ASTM D3120</td>
<td>% wt</td>
</tr>
<tr>
<td>Color, Gardner</td>
<td>ASTM D1209</td>
<td>Gardner</td>
</tr>
<tr>
<td>Water</td>
<td>ASTM D1744</td>
<td>% wt</td>
</tr>
<tr>
<td>Appearance, clear an free of foreign matter</td>
<td>visual inspection</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Toluene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Endo-DCPD</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Iron</td>
<td>ASTM D5708</td>
<td>ppm wt</td>
</tr>
<tr>
<td>Methyl-DCPD</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Endo + Exo-DCPD</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>TCPD</td>
<td>UOP 744</td>
<td>% wt</td>
</tr>
<tr>
<td>CPD codimers</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Freezing point</td>
<td>ASTM D1015</td>
<td>deg.C</td>
</tr>
<tr>
<td>CPD-Butadiene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>CPD-isoprene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>CPD-piperlylene</td>
<td>UOP 725</td>
<td>% wt</td>
</tr>
<tr>
<td>Peroxides</td>
<td>Merck 10011</td>
<td>ppm wt</td>
</tr>
<tr>
<td>Inhibitor (4-TBC)</td>
<td>ISO 8176</td>
<td>ppm wt</td>
</tr>
</tbody>
</table>

Table 1: Analytical Methods
1.5 Applications

There are two general categories of industrial end uses of CPD and DCPD: (1) commodity resins and polymers, which include hydrocarbon resins, unsaturated polyester resins and ethylene-propylene-diene rubbers (EPDM); (2) specialty polymers and fine chemicals, which include cyclic olefin copolymers, flame retardants, agrochemicals, specialty norbornenes, flavor and fragrance intermediates. The majority consumption can be found in the first category.

A good description on these applications can be found in the Kirk-Othmer Encyclopedia of Chemical Technology (1978; 7 (2): 417-429)

2. Responsible Care®

In line with regulations and as signatory of the Responsible Care® principles, producers provide information regarding the storage, handling, use and ultimate disposal of the chemical products they supply. A key document in this respect is the Material Safety Data Sheet. It is an invaluable source of health and safety information, and available in many languages. A copy of the current DOW MSDS for this product should be kept on hand; contact your DOW customer service center for a current copy of the MSDS for the product you are using. For information on specific applications of DCPD, users are urged to contact the customer service center.

2.1 Safety Hazard Information

Because DCPD is flammable and toxic, precautions must be taken to assure that it is safely stored, transported and converted into commercial products. Within production areas DCPD must be isolated from any and all sources of ignition, and personnel must be protected from excessive exposure. See the Material Safety Datasheet for more details. Additional precautions are required to limit contact with air or oxygen in order to prevent peroxide formation.

The tendency of DCPD to form peroxides during storage may be greatly reduced by the addition of phenolic derivatives in order to inhibit oxidative degradation or unwanted polymerization. The use of phenolic derivatives is recommended when DCPD is stored for an appreciable amount of time before being used, thus increasing the chances for contact with air.

As illustrated in Figure 3, at around 140-150°C the formation rate of CPD from DCPD is considerable and, via consecutive Diels-Alder reactions, tri, tetra and higher polymers will be formed. During the first stage of such a polymerization DCPD is sufficiently fluid to remove the reaction heat. However, further polymerization increases the viscosity and reduces convective heat transfer.

If this is allowed to rise uncontrollably, temperatures in excess of 300°C may result, with the consequent explosive formation of gases. These gases, mainly hydrogen, methane and ethane, together with the reactor contents can subsequently form a further explosion hazard. Careful reactor design is therefore required to control the polymerization.
2.2 Flammability Hazard
DCPD is flammable and the Dow DCPD products have flash points between 25-40°C. Pure (100%) DCPD has a flammable range (in air) of 0.9 - 6.3%-vol. and DCPD products are classified as a flammable liquids. However, over the years extensive experience has been gained concerning preventive measures against fire and explosion. The potential for fire or explosion during storage or transport of DCPD products needs to be carefully considered. Examples include:

- Padding with an incombustible gas helps to reduce the occurrence of flammable headspace in shipping and storage containers.
- Ignition sources, including static discharge, should be eliminated in DCPD handling areas.
- Design of plant operating equipment should include the possibility of DCPD containing vapor passing through the explosive zone during changes in pressure, e.g. during the emptying of a vacuum system.

2.3 Inhibition
DCPD reacts with oxygen and may form unwanted products such as brown gums or peroxides. This reaction can be controlled with 4-tertiary-butyl catechol (4-TBC), a common inhibitor for hydrocarbon products such as styrene. However, contrary to other olefins such as styrene, the polymerization of non inhibited dicyclopentadiene via radicals is insignificant for DCPD. In view of its sensitivity to oxygen, inhibition of DCPD and inert gas padding are recommended, preferably combined with an internal floating roof to prevent build up of dangerous peroxides and to preserve good feedstock color.

Figure 5 TBC depletion in DCPD Resin Grade at 40°C

Considering the inhibitor depletion of 4-TBC in DCPD Resin Grade (see figure-5) and the fact that no polymer was formed during laboratory testing, it was concluded that for normal storage periods a dose of 50 ppm will provide sufficient guard against gum and peroxide formation and product degradation.
2.4. Health hazard information

2.4.1 Acute oral
The acute oral toxicity of DCPD is considered moderate. The LD₅₀ reported for albino rats is between 380 and 1000 mg per kilogram of body weight. Small amounts swallowed incidentally as a result of normal handling operations are not likely to cause injury; however, swallowing larger amounts may cause serious injury, even death.

2.4.2 Eye contact
Eye contact with DCPD will likely result in severe pain and slight conjunctive inflammation. Corneal injury is not expected to occur, if contaminated eyes are immediately flushed with flowing tap water for at least 15 minutes.

2.4.3 Skin contact
The dermal LD₅₀ was reported to be between 4371 and 6586 ml/kilogram in rabbits and over 2000 mg/kg in rats. A moderate chemical burn is likely to result from repeated exposure; however DCPD is not likely to be absorbed in acutely toxic amounts.

2.4.4 Vapor inhalation
The vapor pressure of DCPD is approximately 2.0 mm Hg at 20°C; toxic concentrations may occur at room temperature. Since the 4h-LC₅₀ by inhalation for male and female rats is over 2 mg/l (Kinkead) the inhalation hazard of DCPD is therefore classified as harmful.

Kinkead et.al. determined from an 89-day inhalation study that the no-effect level was below 19.7 ppm for rats and about 30 ppm for dogs. The lower no-adverse effect in rats is believed throughout the industry to be the result of an effect which only occurs in male rats exposed to hydrocarbons. Therefore the rat data are not believed throughout the industry to be relevant to man.

Slight transitory eye and/or throat irritation may occur in some humans inhaling concentrations of vapor in the range of 1 to 5 ppm. As a result an occupational exposure limit of 0.5 ppm (3 mg/m³) has been generally accepted by the industry.

Fortunately the odor of DCPD vapor is detectable far below this criterion: two thirds of a test group of six people were able to detect 3 ppb and all six detected 6 ppb.

2.5 Environmental toxicity
Based on the static acute LC₅₀ for fish and aquatic invertebrates DCPD is considered slightly toxic. The bioconcentration potential is moderate in view of the partitioning coefficient (log Kow ~2.9) and soil mobility (log Koc ~3.5). Atmospheric degradation is rapid (t₁/₂: 2-3 hrs) but biodegradation is poor. As a result of the low solubility and
specific gravity (< 1.0 g/cm³) DCPD floats on the water and volatilizes appreciably, despite its boiling point of 170°C. From the data above, it is clear that water solubility (40-100 mg/l) and partitioning data, rather than lexicological data, are the determining factors for the environmental impact assessment.

Notes:
(1) Kow, and Koc are the respective octanol/water and sediments/water partitioning ratios of DCPD.
(2) ratio BOD5:ThOD < 0.05 (biological oxygen demand in five days is less than 5% of theoretical oxygen demand).

2.6 Flammability Control

2.6.1 General Information
The use of unmanned hose holders or monitor nozzles should be considered. Burning liquids may be displaced by flushing them with water in order to protect personnel and minimize property damage. Use water spray to cool fire-exposed containers and fire affected zones until the fire is out and the danger of re-ignition has passed. Accumulation of water should be avoided since DCPD may be carried across a water surface, spreading fire or increasing the chance of contacting an ignition source. Personnel should stay upwind and not enter low areas where gases (fumes) can accumulate.

2.6.2 Flammability
DCPD will burn. Consequently, precautions against fire and explosion that are commonly applied for combustible and flammable liquids should be followed. The flammability properties for DCPD are:

flash point (tag closed cup): ~32°C (25 - 40 °C), auto-ignition temperature: >600°C, lower flammability limit (in air, at atmospheric pressure, at 28°C): 0.8%-vol. It should be noted that liquid spills on hot fibrous insulation material may lead to lowering of the auto-ignition temperature, and possibly resulting in spontaneous combustion.

2.6.3 Explosive Mixtures
During loading and unloading, special attention should be given to avoiding cross contamination of the vapor phases, thus maintaining quality, safety and environmental criteria. DCPD can form a combustible mixture with air at a rather low temperature, and therefore necessary precautions must be taken e.g. repair leaks immediately, ensure that handling areas are well ventilated, install proper facilities to remove spills quickly and pressure test equipment periodically. It is also important to prevent the formation of explosive or combustible mixtures at other than normal pressures and temperatures, i.e. a) higher temperatures and/or higher pressures will lower the Lower Flammability Limit (LFL) and raise the Upper Flammability Limit (UFL), b) during the evacuation step a vapor system may pass through the explosive range.

Before entering or welding empty DCPD storage tanks and other containers, they must be flushed with water and/or steam, followed by nitrogen, and subsequently air in order to
remove monomer vapor. Before entering any DCPD storage tank that has been flushed with nitrogen, an appropriate measurement device should be used to check for sufficient oxygen.

2.6.4 Static Electricity

Electrical charges can build up on poorly conductive surfaces of installed equipment to the point at which the dielectric strength is exceeded and a spark develops. The main preventive measure for static electricity problems is to bond the various equipment parts together and to ground the entire system. DCPD can pick up and hold a static charge during transfer from a tank car to a storage tank. Because of this, the storage tank needs to be well grounded. Submerged filling is recommended for all flammable liquids. The inlet line should terminate at or near the bottom of the tank and should make electrical contact with the tank in order to eliminate uncontrolled electrical discharge.

Operators wearing rubber-soled shoes, especially on certain composition floors made of insulating materials, can pick up considerable static electricity and should exercise appropriate caution.

Observing the above precautions will help reduce problems with static electricity.

2.6.5 Fire Suppression

Fires involving DCPD can be safely extinguished with foam, dry powder, water fog or carbon dioxide. However, water is not an effective extinguishing agent for use on water insoluble monomers such as DCPD. If electrical equipment such as motors, open hot plates, or open electrical switches are involved, foam should be used with caution.

2.6.6 Ignition Sources

There are a wide variety of sources of ignition and because some of them are difficult to avoid, consideration should be given to providing an inert atmosphere as the main measure in order to minimize the risk of fire or explosion of flammable vapors. It seems more prudent to control the atmosphere rather than the need for non sparking tools. The use of a metal measuring tape for tank gauging is an example of improper use of equipment.

2.6.7 Community Awareness

In the event of a fire, the emergency response plan should take into account not only the potential impact on the site operations but also the impact on the neighboring community. The response plan should include notification to local authorities and communications to the public.

2.6.8 Emergency Response Team

Fire fighting crews must take note of hazards unmatched by any other occupation and therefore must take note of the DCPD specific hazards, i.e. flammability and explosion potential above 31°C.
An uncontrolled cracking of DCPD (reverse Diels Alder reaction) with subsequent polymerization may lead to rapid buildup of temperature and subsequent explosive formation of flammable gases. The vapor of DCPD is heavier than air and therefore safe distances must be maintained. Smoke may contain DCPD in addition to unidentified toxic and irritating compounds and therefore requires the use of a self contained breathing apparatus. For a comprehensive set of product data/aspects and personal protection, see also the Material Safety Data Sheet.

2.6.9 Containment
To limit flammability, exposure and environmental hazards, every effort must be made to contain spilled DCPD. Therefore, in the engineering phase, a bund and optionally a remote emergency containment system should be provided for the storage tank and unloading station in order to achieve a limited evaporation surface, better foam effectiveness and improved run-off control of contaminated fire and sprinkler water. Overflow of hydrocarbons from bunds due to addition of fire water can be avoided by installing an underflow weir or siphon. Advise the local Water Authority if spillage has entered a water course or external drainage system.

2.6.10 Foam
For extinguishing a fire and limiting evaporation, Aqueous Film Forming Foam or Alcohol Type Concentrate have been proven to be effective, i.e. that the lower flammability limit is not attained above the layer. Because a foam layer can break down, this function must be watched and maintained. As a few inches of foam are sufficient to smother a fire inside a container, the contained amount of water is unlikely to trigger a so-called slop over; larger amounts may do so.

2.6.11 Water Spray
A water spray has been proven to be the most effective way for product cooling, but its efficiency and effectiveness must be weighed against the risks of spreading DCPD across the water surface, the chance of a slop over when water comes inside the tank, and the possibility of not containing the DCPD within a containment system. Because of its flammability and explosion hazard, DCPD must be prevented from entering sewers. The control of the disposal of deluge and/or spray water is also important because the contained DCPD is an acute hazard both for public sewers and waste water treatment plants.

In case of such a release, Local Authorities must be informed immediately.

2.7 Handling and Disposal

Note: the information in this section is based on extensive experience and data collection, and is expressed in good faith. The Dow Chemical Company accepts no liability for operations not under its direct control. Appropriate and safe handling practices are the responsibility of the customer/user.

Considering the health hazard data of DCPD and its potential to be a harmful environmental contaminant, it is stressed that measures should be taken to prevent emissions to surface and groundwater, air and soil when handling DCPD concentrate.
2.7.1 User label

DCPD is listed in Annex I of the Dangerous Substances Directive (67/548/EEC). In the 22nd adaptation the following hazard classification has been accepted:

- F; R11 (highly flammable), Xn (harmful);
- R20/22 (harmful by inhalation and if swallowed), Xi (irritant);
- R36/37/38 (irritating to eyes, respiratory system and skin),
- N (Dangerous for the environment);
- R51-53 (Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment).

2.7.2 Personal protection

The most significant hazard associated with the handling of DCPD is excessive vapor inhalation. Care must be taken to prevent even short exposure to concentrations such as might be expected from spills or careless handling. The time weighted average exposure must be limited to concentrations below 1 ppm to avoid undesirable local irritation of the eyes and respiratory passages, and systemic effects. Consult the Material Safety Data Sheet for more details on personal protection.

2.7.3 Spill and disposal practice

A small spill of DCPD may be treated with a chemical sorbent for subsequent incineration. Large spills should be contained to prevent entry into any surface or ground water. Vacuum trucks are recommended to remove spills for incineration or recovery.

2.8 Environmental Control

2.8.1 Emergency Plan

Facilities using DCPD should have developed and implemented a comprehensive spill prevention and emergency response plan.

This plan should address:

1. spill detection methods,
2. emergency notification procedures,
3. community contacts for notification and advice on evacuation needs,
4. fire prevention and protection,
5. provisions for spill containment/clean-up,
6. environmental protection,
7. compliance with applicable local regulations or laws.

2.8.2 Spills and Leaks

Because DCPD is only slightly soluble in water and extremely flammable at ambient temperatures, spills and leaks require prompt response to minimize the risk of fire and/or explosion, as well as to limit fugitive emissions. DCPD is toxic to aquatic organisms and therefore surface waters and sewage systems should be protected from spills.
2.8.3 Accidental Release
In the event of a significant spill of DCPD, all non essential personal should be evacuated and all sources of ignition extinguished immediately. After the appropriate personal protective equipment has been issued, the spill can be covered with fire-fighting foam to minimize emissions and the potential of fire hazards. Depending on the volume and location of the spill, it can be recovered by an inert padded vacuum truck or with solid sorbent and placed in appropriate containers for disposal. Spills into surface water may be cleaned up using a skimmer or vacuum system because DCPD floats on water. Spilled DCPD can be removed safely by covering it with a suitable absorbing agent such as sand. However, some absorbing agents, such as untreated clays and micas, may cause an exothermic reaction which could ignite the monomer. Absorbing agents should be tested for their effect on monomer polymerization before they are used on large spills. If the spill is on a hard surface, the area should be scrubbed with soap and water after the bulk of the monomer has been removed. When spills occur within a bund confined area without an impervious base, water should be pumped into the area immediately. This will prevent the monomer from soaking into the ground and will allow it to be pumped off the water layer for later recovery.

2.8.4 Containment Aspects
Storage and handling facilities for DCPD should be designed to contain and control spills from process areas and loading/unloading operations. Soil, surface water, and ground water contamination from a spill of DCPD can be minimized by the installation of curbs, sumps, and impervious containment areas. These areas should be constructed of materials such as concrete and synthetic liners. Under concrete slabs an impermeable liner is recommended and suitable sealants, e.g. epoxy, should be used on cracks and concrete joints.

2.8.5 Waste Classification
DCPD containing wastes are considered hazardous if the flash point of DCPD is below 61°C. Hazardous wastes may include, but are not limited to, process wastes containing DCPD, DCPD contaminated water, soil, debris, and empty unclean containers.

Soil contaminated with DCPD to the extent it has to be treated as hazardous waste should be excavated and transported to a secure hazardous waste treatment or disposal facility. Other materials contaminated with DCPD may be ignitable and should be treated as hazardous until proven otherwise. For contaminated product the preferred disposal options include sending to a licensed incinerator or other thermal destruction device. As a service to its customers, Dow can provide lists of companies that recycle or process DCPD and that handle used drums. Water contaminated with DCPD may be cleaned by air stripping (to remove the bulk of the DCPD), followed by biological treatment and, if required, treated with granular activated carbon. The DCPD vapor should be captured by a collecting system. Containers used to hold DCPD must be drained and then thoroughly cleaned to be considered nonhazardous. Rinse liquid generated from washing should be
collected and properly disposed of. Waste classification and compliance with laws, regional and/or local, are the responsibility of the waste generator.

3. Engineering and Operation

3.1 General Tank Design Aspects

In addition to the precautions for flammable liquids, the maintenance of a uniform temperature, preferably below 30°C, both to minimize Diels-Alder polymerization and to avoid installation of costly emission control technology is recommended. Also an inert / incombustible padding gas is recommended to avoid flammable or explosive mixtures in the vapor space of the tank.

The internal surface of the tank, including safety devices, must be smooth to avoid adhesion of condensed DCPD.

Experience has shown that efficient circulation is important to avoid a temperature gradient in the tank. Inlet, outlet and recirculation connections are required.

Tanks should be designed and constructed in accordance with an appropriate and recognized standard of good engineering practice (e.g. British Standards, German Industry Norms (DIN) and American Petroleum Institute Standards) and should take into account local climate conditions.

3.1.1 Construction materials and tank internals

The standard construction material is carbon steel or stainless steel. Aluminum is satisfactory but will not withstand a fire. Copper will combine with the organic acids and oxidation products present in the monomer. Therefore, copper and copper alloys must be avoided. The resulting impurities will color the monomer. The roof openings above the normal liquid level should be large in diameter and kept to a minimum. By sloping the tanks toward the drains, horizontal tanks can be drained more completely.

Floors of large vertical tanks may be tilted toward a small built-in sump with a bottom drain.

3.1.2 Pressure rating

The design pressure should be to API-620 or equivalent. This sets the specification for the relief system as well as minimizing breathing losses during ambient temperature changes and enabling vapor conservation measures during filling. Containment of breathing losses during a temperature rise of the contents of 20°C should be considered. Preferably the vents should be connected to a vapor collection and recovery or treatment system and thus minimize hydrocarbon emission.
3.1.3 Fire protection

Considerations in site selection and tank spacing include proximity to other flammable material storage facilities, nearby sources of ignition, accessibility for fire fighting, and the impact of a vapor cloud explosion on nearby areas. Fire monitors may be considered in order to provide cooling in the event of an external fire. A flame arrestor should be installed between the tank and any opening to the atmosphere. The installation of a foam chamber or subsurface injection connection is also recommended for automatic fire fighting, particularly on larger tanks.

3.1.4 Uniform temperature control

Efficient mixing is important to achieve a uniform temperature. Therefore, inlet, outlet and recirculation connections are usually located near the bottom of the tank and can be reversed so that the DCPD is pumped from the bottom and discharged through the swing pipe below the liquid surface. If desired, cooling the content from the bottom up can be achieved via the swing pipe, i.e. DCPD can be withdrawn below the liquid surface and returned to the bottom. It is stressed that return of DCPD to the tank should always be below the liquid level in order to prevent static electric charge buildup, and a reliable siphon break should be provided in dip pipes. It is strongly advised to install a temperature measurement that will measure the liquid temperature inside the tank, with added alarms that will trigger action in case of rising temperature inside the tank. If the temperature is rising fast, this indicates that reactions (Diels Alder and reverse reactions) or decomposition of DCPD to CPD is taking place which could lead to rapid pressure buildup and subsequent rupture or explosion of the tank. It goes without saying that in warm climates a chiller will be a minimum requirement to maintain the desired storage condition.

3.1.5 Lines and valves

The following are recommended engineering practices:

a. lines smaller than 25 mm in diameter should not be used,
b. a minimum of flanged connections is preferred because of leak potential,
c. lines should not be buried because of the difficulty of checking for leakage,
d. all lines should be sloped so they can be completely drained for maintenance,
e. newly installed lines should be pressure tested by an industry approved method before installation.

Thermal expansion in blocked DCPD lines exposed to the sun and without relief protection can cause high pressure, which can result in failure of gaskets, pump seals, and pump housings. Excessive temperatures in blocked lines can also cause polymerization. If burial is preferred, the appropriate regulatory requirements to protect soil and ground water should be observed. A dip pipe should extend to the bottom of the tank and be provided with a pinch hole (siphon break). The electrical continuity across connections should be checked to ensure grounding. Lines constructed of carbon steel are acceptable, but copper, bronze, or plastic should not be used. Large lines are usually joined by welded flanges, for smaller lines threaded joints are satisfactory. DCPD can dissolve pipe dope and thus cause product coloration and contamination. To avoid this, the pipe threads can be wrapped with PTFE [poly (per)tetrafluoroethylene] tape.
A fusible air line or equally effective safety shutoff valve should be installed to close off lines in case of excessive external heat. Emergency block valves for isolation of equipment by remote activation may be considered on storage tanks, unloading stations and long pipelines holding large amounts of DCPD. Plug cocks and ball valves lined with fluoro-elastomer give excellent service with stainless steel balls. Gate valves are generally more economical and may be used; however, they are less satisfactory. Lubricated plug cocks and non-lubricated ball-type valves are satisfactory. The piping system should use plug valves rather than ball valves for all manually and infrequently operated valves. Ball valves may trap DCPD that may polymerize, seize the ball and thus make it inoperative. To limit emissions from packed glands, bellow valves may be considered. Drain line valves should be provided with a cap or end-flange. Valves must be protected against freezing, heat shock, or mechanical stress.

### 3.1.6 Pumps

Most pumps are suitable for DCPD, except those having copper, bronze, or plastic parts. Centrifugal pumps with enclosed impellers and mechanical seals are the most widely used, but displacement pumps and rotary pumps are satisfactory. A canned or magnetically driven pump may be considered to comply with tight fugitive emission regulations. All metal should be properly grounded to avoid static accumulation. Because deadheading will cause heat build up and lead to polymerization, a minimum flow line should be installed. The pump and circulation system should allow injection of

- instrument air,
- TBC stock solution
- foam to smother a fire, and
- a diluent, e.g. toluene, to reduce the viscosity of the tank content during a runaway temperature increase.

In addition to mechanical reliability aspects, environmental performance parameters should be considered in the selection process for seals. For mechanical seal components it is recommended to specify stationary face (e.g. tungsten carbide) and rotating face (e.g. carbon). Tandem seals with barrier fluid are recommended.

### 3.1.7 Tank pit

A containment system is a basic requirement for DCPD storage to:

- limit the spreading of a DCPD spill and thus limit the flammability and environmental hazard,
- control run-off during fire fighting,
- provide a barrier against soil and groundwater contamination,
- allow spilled product to be effectively covered with foam.

An under storage leak detection system is recommended.

For containment, always consider the storage size, configuration and hydraulic load due to sprinkler water and rainwater and whether foam will be the standard medium/practice for fire extinguishing. To contain the DCPD in a fire situation, a siphon or under-flow weir may be considered.
3.1.8 Loading and unloading facilities
A remote impoundment for flammables could be considered.

3.1.9 Drainage
Installation design should allow for recirculation and complete drainage, and
subsequently flushing with inert gas. This is especially important when DCPD is stored
for extended periods of time or when equipment is used intermittently.

3.1.10 Accessories
Gaskets and O-rings
For flanged connections at ambient conditions it is recommended to use gaskets of
NBR/aramide or graphite with a metal reinforced rim inside. O-rings in DCPD service
should be made from a co-polymer of fluorinated ethylene and fluorinated propylene.
Rubber or other DCPD soluble materials and PTFE encapsulated O-rings should be
avoided. For gland sealing, graphite (optionally PTFE) is the material of choice.

Filters
Since small amounts of foreign matter may enter a storage tank from various sources, a
filter in the transfer piping between tank and processing equipment is recommended. A
replaceable cartridge or filter is recommended. Suitable materials are polyester and nylon.
Especially for sealless pumps, an inline basket strainer is recommended. The strainer will
have adjacent isolation valves and connections for blowing it clear, for safe removal and
for cleaning.

Flexible transfer hoses
To avoid contamination of the DCPD, the most important aspects for transfer facilities
are easy cleaning and product compatibility. Therefore lightweight aluminum pipe and
swing joints, with seals of fluoro-elastomer are preferred. Composite hoses, which are
static-conductive, and flexible metal hoses (woven metal type) are satisfactory, but they
require more care and attention to keep them properly clean and to prevent damage or
breakage during use. Hoses from fluoro-olefin elastomers give the best service and are
the most widely used of the composite hoses. Neoprene elastomer synthetic hoses do not
have sufficient resistance to aromatics and are therefore not recommended for DCPD
service. Multi-layered polypropylene and PTFE hoses are flexible and chemically
resistant, and are therefore recommended materials. All transfer lines and hose
connections should be properly grounded to prevent build up of static electricity. Regular
preventive maintenance is recommended for flexible transfer lines.

4. Selected Bibliography.

This section includes those literature references and patents that may prove to be of
greatest interest to customers for DCPD products from Dow.
4.1 General References

- Naming and indexing of chemical substances for Chemical Abstracts. Appendix IV from CA 1985 index guide, suffix 146-155.

4.2 Safety and (eco)tox references

- The Dow family of styrenic monomers. The Dow Chemical Co., Midland, MI. Form no. 115-00608-1289X-SA1.

4.3 Aromatic hydrocarbon resins

DCPD concentrate is mostly (co) polymerized thermally or using Friedel-Crafts catalysts with a resin oil type which is rich in reactive aromatics, such as styrene, alfa-methylstyrene, vinyltoluene isomers, Indene and methyl-indene.

The resins, characterized by softening point, color, solubility and unsaturation, are marketed both as liquids and solids.

They are extensively used in adhesives, printing inks, rubber compounding, (hot-melt) surface coatings, mostly to modify specific parameters and rarely used alone.

From the patents listed, one can see that DCPD has been used for considerable time to make various hydrocarbon resins.

- US 2898316 - (531124) Ruhrchemie A.G. Composition comprising an oxygen containing polymer of cyclopenta-diene and wax.
- US 3468837 - (670726) Neville Chemical Company. Soluble, high melting dicyclopentadiene polymer type resins, its process of manufacture and its use in compositions, such as printing inks.
- US 4056498 - (720117) Neville Chemical Company. Production of novel resins and their uses in printing ink compositions.
4.4 Unsaturated Polyester Resins

In particular in the US, DCPD has been incorporated for many years in polyester by using Diels-Alder reaction techniques. **DCPD UPR grade** from Dow specifically meets the requirements of unsaturated polyester manufacturers, but suits other applications as well.

Dow developed a hydrolysis technique to maintain DCPD's tricyclic (C10) structure and to prevent both inefficient maleic anhydride consumption and resin coloring, which are inherent to the addition method. The essence of this technique is to set up reaction conditions for addition of the carboxylic acid to the strained ring of DCPD, a preliminary step to esterification of other components.

From our own experiments with various formulations it was concluded that:

1. the optimum amount of DCPD in the unsaturated polyester resin charge lies in the range of 10-15%.
2. more DCPD can be incorporated with a higher maleic anhydride / phthalic anhydride ratio.
3. less styrene (30-35% vs. 40%) is needed with a higher maleic anhydride/phthalic anhydride ratio to achieve optimum resin properties.

It has been shown that **DCPD High Purity** from Dow is not required to take advantage of this polyester technology because codimers of cyclopentadiene (i.e. with piperylene, isoprene, butadiene and methyl cyclopentadiene) are all functional components in the polyester manufacture. Features of the resulting polyester are exceptional mould resin surface characteristics and higher heat distortion.

The bibliography below illustrates some of the creative syntheses possible with DCPD.

- DE 3807931 - (880310) BASF AG. Crack-resistant unsaturated polyester products.
- DD 256803 - (880525) VEB Lackharz Zwickau. Process for the production of dihydrocyclopentadienylnaleate esters (in German).
4.5 Phenolic resins (precursors and derivatives)

In reaction with crude DCPD, phenol (or phenol formaldehyde novolac) is predominantly alkylated, which in turn can be reacted with formaldehyde, similar to conventional phenol formaldehyde resin manufacture, to yield hydrocarbon-novolacs or (oil soluble) hydrocarbon-resoles. About 90% of the hydrocarbons contained in DCPD Resin Grade from Dow was found to be reactive.

Although sulphuric acid can function both as a condensation and an alkylation catalyst, Friedel-Crafts conditions were found most convenient, as the cyclopentyl ring reacts less readily. With low levels of boron trifluoride, only the strained ring is reactive, and therefore 0.4 %-wt (based on total mass) is recommended.

From the literature below the reader will understand that "novel-bisphenol" (or hc-novolac) opens the door to polycarbonates, polyurethanes and high-tech products. Reaction with cyanogenchloride for instance, produces resins which have excellent dimensional stability and thermal resistance, due to the compact structure of DCPD.

4.6 Epoxy Resins

Novel phenolic resins (including their precursors) may also be considered as the backbones for epoxy resins, to improve electrical properties and resistance to moisture. The effect of higher hydrocarbon content is improved heat distortion, less shrinkage, lower elongation, but lower flexural and tensile strength. It is thought that the listed references will provide a good starting point for research in that application.
4.7 Alkyds, acrylates and latices.

For several decades now, it has been described in industry literature that DCPD, itself, its oligomer or as CPD-maleic anhydride, has been used in solvent based coating manufacture. The publications below indicate that DCPD derivatives currently are key substances in water based coating systems.

- US 2437293 - (480309) Bakelit Corporation. Emulsion containing a drying oil ester resin copolymer.
- US 2593976 - (490422) Interchemical Corporation. Composition comprising ethylcellulose and a fatty oil acid modified alkyd resin.
- US 3088927 - (630507) Velsicol Chemical Corporation. Oil modified alkyd resins modified with a thermal polymer of dicyclopentadiene.
- DE 1234027 - (670209) BASF AG. Process for the production of homo/co monomers.
- US 3627659 - (670711) BASF AG. Radiation treatment of halogen containing olefinically unsaturated ester.
- US 4144212 - (780306) Alcolac Inc. Air-curing polymer latices.

4.8 Specialty Resins

DCPD High Purity from Dow is the feedstock for norbornene and ethylidenenorbornene, the respective monomers for polynorbornene and EPDM rubber production (as a third component to provide a crosslinking site), and may also be used for RIM (reaction injection molding) systems. From cyclopentene, trans-1,5-poly-pentenamer rubber (TPR) was developed to suit various rubber applications, including tyres, but the product has not yet been commercialized. For above applications, CPD is actually the building block and obtained via monomerisation of DCPD, a conversion step which is mostly an integral part of the production process. For process economy, product quality and handling requirements, DCPD High Purity from Dow is, therefore, the preferred feed. In particular the process chemistry is reviewed in these selected literature items.

• Graulich, W., et. al., Bayer AG, Make new rubber from CS's. Hydrocarbon Processing. 1972; 71-75.

4.9 Specialty Intermediates
DCPD and its monomer are also important base materials for the manufacture of: plasticizers, anti-oxidants, fragrances, curing agents, fuel and lubricant additives, pyridine and oxo-products, as can be noted from the following literature list.

• GB 737124 - (550921) Shell Company. Complex compounds of iron carbonyl and cyclopentadiene and their use in fuels and lubricating compositions.
• Cornils, B. & Payer, R., Ruhrchemie A.G. Dicyclopentadiene derivatives - important compounds. Chemiker Zei-tung. 1974; 98: 2, 70-6.
• GB 2028314 - (800305) Chemische Werke Lowi. A process for the preparation of dicyclopentadiene \([2,2'-\text{bis}(4\text{-alkyl-6-t-butyl phenols})]\).
• DE 3707911 - (880331) Deutsche Texaco A.G. New bicyclic amine catalysts for curing polyurethane.

4.10 Upgrading / Monomerization.
For specialty resins and specialty intermediates, CPD or DCPD with over 98% purity is preferred, but these are commercially not available. A plausible explanation would seem to be the requirements for storage and transportation. To produce this quality/demand economically it is felt that the technology, mentioned in the references is best installed at the user's location.

• GB 1261566 - (720126) Hooker Chemical Corporation. Cracking dicyclopentadiene to mono cyclopentadiene.
• DE 2542625 - (760422) Shell Internationale Research Maatschappij B.V. Vapor phase cracking of dicyclopentadiene to cyclopentadiene.


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