DVB
Cross-link a variety of materials for improved thermal, physical, and chemical properties

Divinylbenzene
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The versatile cross-linking agent for improving material properties

Divinylbenzene (DVB) is an extremely versatile cross-linking agent that also improves polymer properties. As a result, it has been used to manufacture adhesives, plastics, elastomers, ceramics, biological materials, coatings, catalysts, membranes, pharmaceuticals, specialty polymers, and ion exchange resins.

It is also important that just a small amount of DVB is needed to improve both chemical and physical properties. This efficiency in use allows you to gain selected property improvements without hindering others.

In short, DVB allows you to create materials not otherwise possible and enhance the properties of existing materials in many ways.

For example, when used to cross-link polystyrene, DVB increases solvent resistance, heat distortion, impact strength, tensile strength, and hardness. And as little as 0.5% divinylbenzene in a styrene polymerization makes the polymer insoluble. However, polymers containing low amounts of divinylbenzene will swell as much as 20 to 40 times their original volumes. Increasing amounts of divinylbenzene reduce the swelling until it is almost nonexistent at the 10% DVB level.

Dow offers three grades of DVB to best match your needs

Dow recognizes that your requirements for DVB may not always be the same in every application. That’s why we offer three levels of DVB concentration, allowing you to balance economy with functionality. For the greatest economy on an active ingredient basis, DVB-55 is your best choice. DVB-63 and DVB-HP (80% DVB) work best when you need high levels of dual double bond functionality to cross-link vinyl polymeric systems with the least amount of material. DVB-HP should also be considered when higher concentrations of ethylvinylbenzene (the major complementary component in these DVB products) do not provide any additional benefits—even though the ethylvinylbenzene will react with most unsaturated systems.
### Typical Chemical Analysis and Structural Formulae

<table>
<thead>
<tr>
<th>Structural Formula</th>
<th>DVB-55</th>
<th>DVB-63</th>
<th>DVB-HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Divinylbenzene¹</td>
<td>56%</td>
<td>63.5%</td>
<td>80%</td>
</tr>
<tr>
<td>Meta-Para Divinylbenzene isomer ratio</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Total Ethylvinylbenzene²</td>
<td>43.0%</td>
<td>35.5%</td>
<td>19%</td>
</tr>
<tr>
<td>Meta-Para Ethylvinylbenzene isomer ratio</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Diethylbenzene</td>
<td>&lt;0.05%</td>
<td>&lt;0.05%</td>
<td>&lt;0.05%</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>&lt;0.04%</td>
<td>&lt;0.04%</td>
<td>&lt;0.04%</td>
</tr>
<tr>
<td>Benzene content</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>t-butyl catechol inhibitor</td>
<td>900-1100 ppm</td>
<td>—</td>
<td>900-1100 ppm</td>
</tr>
<tr>
<td>Color (Gardner)</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Polymer</td>
<td>&lt;5 ppm</td>
<td>&lt;5 ppm</td>
<td>&lt;5 ppm</td>
</tr>
</tbody>
</table>

¹These typical analyses are intended to serve as a guide only and not as specification limits.
²Divinylbenzene CAS #:108-86-1
³Ethylvinylbenzene CAS #:108-106-3
N.D. = Not detectable with current instruments (<50 parts per billion)
Properties of Styrene/Divinylbenzene Copolymers

The increase in heat distortion temperature of styrene/divinylbenzene copolymers is linear with increasing divinylbenzene content, and is approximately equivalent to 3.3°C for each 1% increase in divinylbenzene.

Like tensile strength, impact strength increases with the first few % of divinylbenzene, and then falls off rapidly. Copolymers with high divinylbenzene content are very brittle.

The tensile strength increases with the first 5% divinylbenzene, and then drops off rapidly to a very low value.

Hardness increases steadily with increasing divinylbenzene concentration.
## Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Temp. °C</th>
<th>(DVB-55)</th>
<th>(DVB-63)</th>
<th>(DVB-HP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>130.191</td>
<td>130.191</td>
<td>130.191</td>
<td></td>
</tr>
<tr>
<td>Boiling Point, °C at 760 mm</td>
<td>195</td>
<td>197</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Pseudocritical Pressure, P, atm.</td>
<td>34.2</td>
<td>34.4</td>
<td>34.9</td>
<td></td>
</tr>
<tr>
<td>Pseudocritical Temperature, t, °C</td>
<td>425</td>
<td>427</td>
<td>432</td>
<td></td>
</tr>
<tr>
<td>Vapor Density (air = 1)</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure, mm Hg</td>
<td>0</td>
<td>0.07</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>25 0.6</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 3.0</td>
<td>2.9</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75 11.7</td>
<td>11.4</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 36.2</td>
<td>35.0</td>
<td>33.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>125 93.8</td>
<td>91.3</td>
<td>86.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150 212.4</td>
<td>207.1</td>
<td>197.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>175 431.2</td>
<td>422.3</td>
<td>406.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 801.3</td>
<td>788.2</td>
<td>764.8</td>
<td></td>
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<tr>
<td>Heat Capacity, cal./(g °C)</td>
<td>25 0.42</td>
<td>0.42</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 0.912</td>
<td>0.9151</td>
<td>0.921</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 0.908</td>
<td>0.9111</td>
<td>0.9167</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 0.904</td>
<td>0.9070</td>
<td>0.9124</td>
<td></td>
</tr>
<tr>
<td>Density, g/cc (in air)</td>
<td>20 0.9123</td>
<td>0.9151</td>
<td>0.921</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 0.9084</td>
<td>0.9111</td>
<td>0.9167</td>
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</tr>
<tr>
<td></td>
<td>30 0.9044</td>
<td>0.9070</td>
<td>0.9124</td>
<td></td>
</tr>
<tr>
<td>Density, lb/gal</td>
<td>20 7.61</td>
<td>7.64</td>
<td>7.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 7.58</td>
<td>7.60</td>
<td>7.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 7.53</td>
<td>7.57</td>
<td>7.61</td>
<td></td>
</tr>
<tr>
<td>Flash Point, °C, tag closed cup</td>
<td>68 (155)</td>
<td>69 (156)</td>
<td>70 (158)</td>
<td></td>
</tr>
<tr>
<td>Auto Ignition Temp., °C (°F)</td>
<td>505 (941)</td>
<td>494 (921)</td>
<td>470 (878)</td>
<td></td>
</tr>
<tr>
<td>Heat of Vaporization, Hv, cal/g</td>
<td>25 101.3</td>
<td>96.9</td>
<td>94.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>@ Normal b p 83.8</td>
<td>79.4</td>
<td>77.4</td>
<td></td>
</tr>
<tr>
<td>Refractive Index, D-Line</td>
<td>25 1.5585</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Solubility in Water, %</td>
<td>25 0.0052</td>
<td>0.0052</td>
<td>0.0052</td>
<td></td>
</tr>
<tr>
<td>Water in, %</td>
<td>25 0.054</td>
<td>0.054</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>Viscosity, cps</td>
<td>25 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Cubical Coefficient of Expansion,</td>
<td>20 8.66 x 10⁴</td>
<td>8.66 x 10⁴</td>
<td>8.65 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>ig/cc °C</td>
<td>30 8.74 x 10⁴</td>
<td>8.74 x 10⁴</td>
<td>8.70 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>pale yellow</td>
<td>pale yellow</td>
<td>pale yellow</td>
<td></td>
</tr>
</tbody>
</table>
DVB is used to modify the properties of a wide variety of materials. Listed below are just a few examples of how DVB can be applied. New applications continue to be found for this versatile cross-linking agent. For an even broader overview of this monomer’s usefulness, we’ve included a list of patents and references for various applications of DVB later in the brochure.

Adhesives
DVB has been found to improve the high temperature strength of adhesives used to bond aluminum to aluminum. Used in an acrylic hydrosol to bond Bakelite resin and polyester film, DVB was found to increase creep rupture time dramatically. DVB has found utility in cross-linked styrene/butadiene polymers used for caulks and mastics for the construction industry.

Biological
DVB has been used to produce cell culture micro-carrier beads. These resulting beads have capacity comparable to dextran beads but swell less. They also have a tighter size distribution and can be regenerated. DVB has also been incorporated in a hydrogel for slow nutrient release fertilizer.

Catalysis
DVB has been used to create a hydrophobic foam for use as a hydrogen-water exchange catalyst. In another instance, a catalyst was bonded to a DVB-containing copolymer for hydroformylation of C12 alpha-olefins with CO and H. DVB has also served as a catalyst for hydrolyzing nitriles to amides.

Ceramics
In a polymer impregnation system, DVB has improved both the physical and mechanical properties of fired clay bodies. It’s also been used as part of a treatment to impregnate and harden carbonizable material to produce a composite C material.

Chromatographic Resins
DVB has been used in the production of reversed-phase packings for liquid chromatography. Highly cross-linked polystyrene packings have been shown to function under extreme conditions of high pressures and temperatures. Ion exchange chromatography (IEC) is applicable to the separation of almost any type of charged molecule, from large proteins to small nucleotides and amino acids.

Coatings
DVB has been used as part of a system for bonding a layer of phosphonitrilic polymer to rubber to improve the surface properties of rubber goods for biomedical applications. It has also been used to create a photocurable protective coating for wood, metal, glass, and plastic.
Combinatorial Chemistry

Combinatorial Chemistry involves the rapid synthetic assembly of structural building blocks in various possible combinations to produce large libraries of compounds for drug screening purposes. Styrene and DVB have been copolymerized and then functionalized to produce microporous solid phase supports to which library members or reagents may be attached.

Composite Plastics

Composite plastics generally are composed of a reinforcing glass fiber and a thermosetting resin such as an unsaturated polyester. DVB has been used to produce low-shrink, curable, fiber-reinforced molding compositions (SMC/BMC). Parts produced with these compositions have been at higher production rates with exceptional smoothness and enhanced physical properties.

Elastomers

DVB helps promote thermoplastic rubber with good moldability, heat distortion properties, and hardness. It also increases the skid-resistance of some rubber compounds and improves the adhesion of rubber to steel, organic, or inorganic filaments. DVB has also been used to improve the adhesive tear strength and elongation properties of rubber-based sealants.

Electrochemical

DVB has increased the electron sensitivity of photomasks for electron-beam lithography and has been used in a gelation agent for alkaline batteries to improve storage stability. It has also improved the properties of electrostatic image toners.

Ion Exchange

DVB is used in a wide variety of ion exchange materials for the selective recovery or removal of materials from fluid streams. It has been used to coat zeolite to improve the effectiveness of organic and heavy metal removal. And in producing ion exchange resin beads, DVB reduces bead swelling, increases bead strength, and improves water retention and capacity.

Membranes

DVB has been used in the preparation of electrolysis diaphragm and piezodialytic transport membrane materials.

Optical Applications

Plastics have found wide utility in the production of ophthalmic lenses. A growing use is in photochromic lenses. These lenses darken outside, in the presence of UV light, and lighten indoors. DVB, along with other monomers and dyes, have been used to produce lighter and thinner photochromic lenses.

Pharmaceutical

DVB is used to create polymers for enzyme and coenzyme immobilization and those to which biologically active proteins, such as penicillin acylase, may be bound. In dental cement and prosthesis materials, DVB helps increase hardness, abrasion resistance, and bending resistance.

Polymer Synthesis

DVB has been used to graft monomers to textiles to produce waterproof fabrics, and to enhance the radiation grafting of polymers such as styrene and polyolefins. It is also used to create the interpenetration polymer networks between polyurethane and methyl methacrylate, thereby increasing tensile strength, hardness, and glass transition temperature of the network. It is also highly efficient in coupling living polymers with polyvinyl aromatic compounds.
Plastics
DVB is used extensively in the plastics industry to cross-link and modify materials and to aid in copolymerization. It can also increase stress crack resistance, resistance to some chemicals, heat distortion, hardness, impact strength, and surface processibility. DVB helps improve the thermal stability of epoxy resin compositions. In the presence of an acid catalyst, it is used to cure phenol-formaldehyde resins and in compositions to seal porous metal castings and make them chemically resistant to halocarbons.

Reprography
Polymeric toners are the dry inks used in the majority of existing copy machines. DVB has been used in the polymerization of some toner resins, imparting enhanced melt properties.

Rubber
Synthetic rubber is any one of a group of man-made elastomers that approximate one or more of the properties of natural rubber (polyisoprene). DVB has been used in Styrene-Butadiene copolymers (SBR) as adhesives and as processing aids in the extrusion of general purpose rubbers. Rubbers used as impact modifiers such as M ethacrylate-Butadiene-Styrene (MBS) have been improved with the inclusion of DVB.

Star Polymers
A star polymer is composed of star macromolecules which are defined as: macromolecules containing a single branch point from which linear chains (arms) emanate. DVB has been used to produce star polymers in a synthesis proceeding by the addition of divinylbenzene to a living cationic polyisobutylene. Such molecules have found utility as motor oil viscosity modifiers also known as viscosity index improvers.

Miscellaneous
- When paraffin is cross-linked with DVB, an additive is created that lowers the filterability temperature of middle distillates such as diesel fuel.
- A vinyl polymer prepared with DVB produces a sealer for consolidating porous subterranean formations.
- Solid makeups containing volatile oils have been created using DVB in an encapsulating resin.
- A copolymer containing DVB was used to recover trace uranium from sulfuric acid containing organic matter.
- DVB added to styrene increases the rate of radionuclear polymerization in concrete. In addition, DVB increased the thermal and mechanical stability of the resulting concrete.
Handling and Storage (including inhibitor handling)

The prevention of polymer development—and runaway polymerization—is generally the greatest concern in the storage of DVB. Prevention of color formation is also important, but this is normally caused by contamination such as rust and water. The most important factors in maintaining a long shelf life for DVB are low temperatures, adequate inhibitor levels and oxygen content, and the use of proper construction materials for storage and handling equipment. Good, basic housekeeping practices are also important. Listed below are general guidelines.

1. Conduct regular equipment inspections.
2. Repair leaks immediately.
3. Maintain good ventilation.
4. Install proper facilities to remove spills quickly.
5. Test pressure equipment periodically.
6. Eliminate all possible ignition sources.

Inhibition of DVB

Dow adds TBC (4-tert-butylcatechol) to DVB to inhibit polymer formation and oxidative degradation during shipment and subsequent storage. If sufficient oxygen is present, TBC prevents polymerization by reacting with oxidation products (monomer peroxy-free radicals) in the monomer. However, in the absence of oxygen, polymerization will proceed at essentially the same rate as if no inhibitor were present.

TBC is highly recommended as a storage inhibitor for DVB. It imparts no color, but does require a minimum of 15 ppm oxygen in the monomer to make its inhibitory capability effective. DVB is shipped with a TBC level of 900–1,100 ppm. This level of inhibitor is normally effective in preventing incipient polymerization for 30 days at a maximum temperature of 80°F, assuming the critical O₂ saturation of 28–30 ppm is maintained. If longer storage times are required, special precautions will be necessary.

To prevent runaway polymerization of stored monomer, the inhibitor level, the temperature of the storage facility, and the oxygen content of the monomer should be carefully monitored. Oxygen content is the critical factor in most situations.

The minimum recommended concentration for TBC in divinylbenzene is between 400–600 ppm. This level should be checked at regular intervals (see table on page 11 for a suggested maintenance schedule). Additional inhibitor should be added as required to ensure maximum safety and storage stability.
Suggested Storage Maintenance Schedule for DVB

<table>
<thead>
<tr>
<th>Checkpoint</th>
<th>Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibitor analysis</td>
<td>Monthly - Weekly if stored above 80°F</td>
</tr>
<tr>
<td>Polymer analysis</td>
<td>Monthly - Weekly if stored above 80°F</td>
</tr>
<tr>
<td>Color</td>
<td>Monthly</td>
</tr>
<tr>
<td>Monomer temperature</td>
<td>Daily</td>
</tr>
</tbody>
</table>

Storage Tank Polymer

Inspection points for polymer:
1. Air vent At least quarterly
2. Roof Yearly
3. Sides Yearly
4. Floor Yearly
5. Vacuum pressure relief At least quarterly

Date of last filling Running log
Volume before filling Running log
Volume after filling Running log

Standard inhibition levels in DVB

The time required for TBC concentrations to fall to a dangerously low level varies greatly for different storage and handling conditions. Most importantly, if the inhibitor has been depleted and polymerization has already begun, TBC should be added immediately, and The Dow Chemical Company or its representative should be notified as soon as possible (call 1-989-636-4400). If unstable monomer is not treated promptly, it may become unsalvageable and may also cause serious consequences (see Polymerization of Stored Monomer, page 18, for more information).

Special cases where inhibitor removal is desired

In special cases, you may want to remove the inhibitor. This can be accomplished by running the DVB through a bed of alumina. Contact Dow for further information and suggested cautions regarding this subject for your particular application.

Other factors affecting inhibitor level

Other factors that affect the depletion of TBC are heat, caustic, and exposure to alumina or ion exchange resin beads. In hot climates or where temperatures greater than 80°F are normally encountered, the monomer bulk storage installation should be refrigerated.
In addition, drums of monomer should not be kept in the sun. As soon as monomer is received, drums should be placed in a cool, shaded area. In very hot weather, drums can be temporarily cooled by water spray. It is advisable to keep monomer inventories to a minimum during hot weather, and to use drums in the order they are received so that monomer is not stored any longer than necessary.

Oxygen requirements of TBC

Air presents a very complex problem in the storage of DVB. TBC is not an effective inhibitor for DVB in the complete absence of dissolved oxygen. However, excessive amounts of oxygen in the storage tank may lead to other serious storage and handling problems.

Monomer vapors above the liquid level in the tank are uninhibited. These uninhibited vapors and condensed monomer droplets are readily oxidized by oxygen from the air. These droplets, containing oxidation products, will polymerize quite rapidly and will adhere to the rusted, porous surfaces of unlined steel tanks. They appear in the form of coatings and stalactites, or “polymer icicles,” on the roof and sidewalls above the liquid monomer. The same condition, though less severe, will also occur in lined tanks.

The polymer deposited under these conditions will be discolored, cross-linked, and high in peroxides, aldehydes, and other oxidation products. Deposits of contaminated polymer will eventually produce serious color and polymer problems in monomer stored under air in unlined steel tanks. Therefore, do not allow mechanical structures in the top part of the storage tank as they will collect these impurities.

Polymer deposits in tanks also cause difficult removal and cleaning problems. If stalactites are allowed to grow, their weight may even damage the roof or roof-supporting structure of large vertical storage tanks.

However, the complete elimination of oxygen from the vapor area will lead to depletion of dissolved oxygen from the liquid monomer. If this dissolved oxygen is not replaced and is allowed to drop below 15 ppm, the TBC inhibitor will become ineffective and rapid polymerization — runaway polymerization — may take place (see Polymerization of Stored Monomer, page 18).

Polymer analysis and dissolved oxygen

Polymer formation can result from insufficient TBC or insufficient dissolved oxygen. An effective test to determine whether polymer is forming in the monomer is ASTM Method D-2121. This test, used in conjunction with the TBC test for inhibitor level, provides a quick means of monitoring monomer condition on site.

Addition of TBC to stored monomer

Add additional inhibitor when the level of TBC falls below the minimum specification level. The TBC content of DVB in storage should never be allowed to be depleted below the 400-600 ppm level.

The storage tank (or drum) should always be recirculated (or mixed) after inhibitor is added. This action ensures a uniform mixture of TBC and monomer. The tank should also be aerated as necessary.

The relatively small quantities of TBC required to raise the inhibitor level in stored monomer can be easily added by using a concentrated stock solution in the monomer.

A TBC concentrate for use in increasing the inhibitor level in DVB can be prepared by dissolving 704 grams of pure TBC in 1 gal. of divinylbenzene monomer (186 gram/liter). At this concentration, 100 cc of the above concentration will raise the level of inhibitor 100 ppm in a drum of divinylbenzene having a net weight of 410 pounds.
A specific bulk storage layout must conform to insurance underwriters’ codes as well as to local fire and building regulations. Decisions concerning distances to power lines, buildings, other tanks, piping, and property lines, as well as diking, and other protection requirements, are usually dictated by these codes and regulations.

Tanks

DVB can be stored for relatively long periods if simple, but carefully prescribed, storage conditions are met. In addition to the usual precautions taken with combustible liquids against fire and explosion hazards, you must prevent conditions conducive to the formation of polymer and oxidation products. This can be accomplished by designing and constructing a bulk storage system that prevents excessive temperatures and contamination of the monomer in frequently used lines and other equipment (see page 15).

Black-iron storage tanks are generally the most economical for DVB, and vertical storage tanks are often used for large-volume storage. Horizontal tanks are also satisfactory for bulk storage, but these are generally used for smaller installations.

A self-supporting, dome-type roof is recommended for vertical storage tanks. This type of construction simplifies the installation of linings, and also permits rapid drainage of uninhibited condensed vapors back into the liquid monomer, thus reducing the polymer and stalactite problem. The roof and sidewall openings above the normal liquid level in the tank should be large in diameter, and kept to a minimal number. Large diameter openings are easily lined and can often serve dual-service purposes.

Inlet and outlet lines for vertical tanks are usually located near the bottom. If you use external refrigeration, good mixing can be accomplished if the inlet and outlet lines are kept as far from each other as possible. In addition, an elbow on the inlet line inside the tank helps to direct cooled fluid upward for better temperature control of the stored DVB. The discharge should always be below the liquid level to prevent static buildup. Eddy currents induced by temperature differences between the chilled monomer and the stored monomer lead to relatively uniform mixing.

Tank linings work well to control or reduce polymer and stalactite formation. A tight, nonporous, non-wettable, and smooth tank lining prevents retention and attachment of the condensed uninhibited monomer droplets. As a result, the monomer drains quickly back into the pool of inhibited liquid monomer before polymerization can take place.
Monomer Storage Installation

NOTES:
1. All Safety, Venting, Devices & Nos. Grounding Per Local Codes
2. Piping/Process, As Indicated on Equipment

NOTES:
1. Piping/Process,
2. Vacuum Pressure
3. Piping/Process,
4. Vacuum Pressure

Dial Thermometer

Grounding Antenna Clamp

Dike
Pumps

Pumps made of most materials are suitable for DVB, except those made of copper or plastic. Centrifugal pumps with enclosed impellers and mechanical seals are the most widely used, but displacement pumps are also satisfactory.

Make sure that pumps are not allowed to run when valves are closed. The heat evolved by pumping against a “deadhead” may be enough to polymerize monomer in the pump and cause contamination.

Totally enclosed, fan-cooled pump motors are acceptable. Their associated switching gear should be of an approved type as listed in the National Electrical Code, with particular attention given to articles 250, 500, 501, and 515, and sections covering Class 1, Division 2, locations. All metal should be properly grounded to avoid the danger of static charge buildup.

Installation design should allow for complete drainage of the storage system, and recirculation of the monomer through the system. This is especially important when equipment is in intermittent service or where monomer is stored for extended periods.

Lines and valves

Thermal expansion in blocked DVB lines exposed to the sun and without relief protection can cause high pressures which can result in failures of gaskets, pump seals, and pump housings. Lines should also be laid out to allow for complete drainage and should be blown out with air after material transfers.
The lines may be constructed of iron or galvanized pipe. Do not use copper or bronze. Oxidation products of these metals can interfere with polymerization. Transfer lines are typically joined by welded joints or flanges, but threaded joints are also satisfactory. Pipe dope can be dissolved by monomer, causing discoloration and contamination. You can avoid this by wrapping the pipe threads with plastic tape coated with Teflon resin.

You can fill the storage tank from the bottom or top with a line extending to the bottom (DVB should not be allowed to fall through free air space in the tank due to the possibility of static buildup). The inlet line should always be at the opposite end of the tank from the outlet line. This will facilitate thorough mixing in the storage tank when new monomer or inhibitor is added. Thorough mixing is further assisted by directing the flow of the incoming monomer up into the monomer body.

You should also include separate drain lines—properly valved and closed—to allow for complete drainage when necessary. Drainage from horizontal tanks can be assisted by sloping the tanks toward the drains. Floors of large vertical tanks can be tilted toward a small built-in sump with a bottom drain.

All valves below liquid level should be steel or ductile iron to prevent breakage from freezing or mechanical stress. Lubricated plug cocks and non-lubricated ball-type valves are satisfactory. Plug cocks and ball valves lined with Viton fluoroelastomer give excellent service with stainless steel balls and are highly recommended for DVB service.

Gaskets

Manhole covers for cleaning or sampling should have gaskets made of Viton fluoroelastomer or Teflon resin. In addition, Dow recommends all gaskets used in handling DVB be made of these materials. Listed below are pump seals and gaskets which have proven satisfactory in DVB service. Similar materials from other manufacturers may work equally well.

Pump Seals:

- John Crane Type 9T
  - Teflon resin V wedge with carbon face seal
  - Runs against carbon seat
  - Stainless steel hardware

- John Crane Type 8IT
  - Viton fluoroelastomer O-ring with carbon face seal
  - Runs against tungsten carbide seat
  - Stainless steel hardware

- John Crane Type 20R
  - Glass-filled Teflon resin with carbon face seal
  - Runs against tungsten carbide seat
  - Stainless steel hardware

Gaskets:

- Flexitalic 31055 flanged joint spiral wound with asbestos filler and inner ring. Flexitalic Gasket Co., 151 Heller Place, Bellmawr, NJ 08031. Phone: 609-931-2500.
- Union BS2131 Grade A BS1832, 1/16-inch compressed. James Walker Mfg., 511 West 195th Street, Glenwood, IL 60425.

Breathers

Air-blanketed, non-pressurized DVB storage tanks should be fitted with approved vents according to local codes. You should also install additional venting facilities—for both pressure and vacuum relief—to protect the tank in case there is a sudden pressure buildup, or open vents are plugged. Frangible safeties or vacuum-pressure safety relief valves are recommended for this purpose on smaller units. On larger storage facilities, both manhole emergency relief venting for pressure and a vacuum-pressure relief valve are highly recommended to assure protection against tank collapse. In addition, inspect all vents at least every six months for polymer plugging.
Level indicators
Float-type, dial-reading gauges are acceptable, but for remote readings, flange-mounted differential pressure transmitters are recommended. All storage tanks should contain either a local temperature indicator, or a temperature sensor for remote reading.

Flexible transfer hoses
Composition hoses, which are static-conductive, and flexible metal hoses are widely used. Flexible metal hoses (woven-metal type) are the most satisfactory, but require more care to keep them properly cleaned. They also require added attention to prevent damage or breakage during use.

Hoses made of Viton fluoroelastomer give the best service and are the most widely used of the composition hoses. Neoprene elastomer synthetic hoses do not have sufficient aromatic resistance for DVB service.

Never allow monomer to stand in any of the composition hoses. Monomer can attack the interior of the hose, shortening hose life and causing monomer contamination. Completely remove all residual monomer and thoroughly clean all transfer lines in intermittent service to prevent this source of potential contamination. Preventive maintenance for flexible transfer lines is recommended. These lines should be carefully inspected to determine their structural condition and cleanliness before being used in DVB service.

Of course, all transfer lines and hose connections should be adequately grounded to discharge static electricity safely.
All polymer buildup on the inside of a storage tank should be removed. This can be done by draining the tank completely and then discharging live steam into the open tank for four to five days. The condensate water must be removed from the tank during the heating process to ensure that all tank surfaces are adequately heated. This will harden polymer formations so that they can be removed by mechanical means.

**NOTE:** The tank must be tested and found to be free of harmful or flammable vapors before entry is made.

Copper-containing alloys should never be used in tank storage and handling equipment—oxidation products from copper alloys can interfere with normal polymerization. Rubber parts also should be avoided because monomers are solvents for natural rubber and most synthetic rubbers.

**Reducing oxidation and side reactions during storage**

To reduce oxidation and hold side reactions to a minimum, stored monomer must be kept cool. Depending on the storage location, various methods can be used, including refrigeration, reflective painting, and shading.

**Refrigeration:** Large aboveground tanks with a low throughput or turnover rate should be insulated and cooled by external refrigeration. If refrigeration is used, circulation of the storage tank contents is required.

**Reflective Painting:** Painting exterior storage tanks with either white or some other light-reflecting paint also minimizes the absorption of sunlight, thereby reducing heat gain.

**Shading:** Slatted shade in an open area where ventilation is assured has proved satisfactory for the protection of small aboveground tanks, pumps, filters, and other handling equipment.

**Containers**

The type of container in which DVB is shipped and stored is very important to monomer purity and stability. Lined and unlined black iron, aluminum, and stainless steel containers are all satisfactory, and typically used to store and transport DVB. Avoid copper and copper-bearing alloys such as brass and Monel alloy.

The oxidation products of copper are picked up by DVB and by the organic oxidation products present in the monomer. This action yields soluble copper salts which can interfere with the polymerization. The presence of copper salts can be detected by the greenish-blue color they sometimes impart to the stored monomer.
Some common reagents such as sulfuric acid, phosphoric acid, hydrochloric acid, iron chloride, and other metallic halides catalyze a violent polymerization reaction of DVB. Before refilling used containers, make sure they are inspected and cleaned to remove reagent residues, or old monomer-containing polymer and oxidation products that could cause contamination or reaction.

The importance of storage temperature

Other factors that affect the depletion of TBC are heat, caustic soda, and exposure to alumina and ion exchange beads. Temperature in the monomer storage area should not be allowed to exceed 80°F for DVB. In hot climates or during hot seasons where temperatures exceed these limits, the monomer bulk storage installation (or stored drums) should be refrigerated.

Drums of monomer should not be kept in the sun. As soon as monomer is received, it should be placed in a cool, shaded area. In very hot weather, drums can be temporarily cooled with water spray. It is advisable to keep monomer inventories to a minimum during hot weather, and to use drums in the order they are received so that monomer is not stored any longer than necessary.

Recommended shelf life

The table below gives the approximate shelf life of DVB under maximum ambient storage temperatures, assuming TBC and dissolved oxygen concentrations are maintained above the minimum levels. Refrigerated storage will significantly extend the shelf life of DVB.

### Recommended shelf life of DVB (all grades)

<table>
<thead>
<tr>
<th>Storage Temperature</th>
<th>Storage Time</th>
<th>Aerate Within</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;40°F</td>
<td>12 months</td>
<td>6 months</td>
</tr>
<tr>
<td>40°F–50°F</td>
<td>8 months</td>
<td>6 months</td>
</tr>
<tr>
<td>50°F–60°F</td>
<td>4 months</td>
<td>4 months</td>
</tr>
<tr>
<td>60°F–70°F</td>
<td>2 months</td>
<td>2 months</td>
</tr>
<tr>
<td>70°F–80°F</td>
<td>1 month</td>
<td>1 month</td>
</tr>
</tbody>
</table>
The shelf life of stored DVB can also be extended with timely aeration. A 5–10 minute air sparge is recommended on a monthly basis for drums and pails stored at temperatures between 70°F and 80°F. DVB containers stored at temperatures from 40°F–70°F need to be aerated according to the table. With aeration and maintenance of p-tert butylcatechol (TBC) level above 400–600 ppm the clock is effectively reset to the recommended storage times.

**Polymerization of stored monomer**

During the first stages of polymerization, the monomer is sufficiently fluid to remove excess heat by convection. But further polymerization increases viscosity and reduces convective heat transfer, allowing temperatures to build. Toward the end of polymerization, the rate of heat evolution decreases because monomer is depleted. Thus, most of the difficulty with high excess temperature occurs near the middle of the polymerization cycle—specifically, between the 30% to 60% conversion level. Of course, the temperature of polymerization, purity of the monomer, and other physical and chemical factors all influence the duration of polymerization and the extent to which the storage temperature will rise.

However, the polymerization process is autocatalytic in nature—any temperature rise accelerates the rate of polymerization which, in turn, increases the rate of heat evolution. Eventually the reaction may become explosive, especially in closed containers where the vapor pressure of the monomer builds up rapidly. In addition to the hazards involved, the molecular weight or viscosity grade of the resulting polymer will be lower than that anticipated from the average ambient temperature.

**Handling runaway polymerization**

Runaway polymerization can occur spontaneously in storage tanks. Depending on the quantity of material in storage, serious consequences may result. Premature polymerization of stored monomer can be prevented by closely monitoring the temperature, inhibitor level, and oxygen content of the monomer.

Appropriate action will be an on-site decision, and will be determined by the stage of polymerization. For specific information, call the Dow Emergency Response Group at 1-989-636-4400.
### Flammability Properties of Divinylbenzene

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB-55</td>
<td>Flash point, tag closed cup</td>
<td>155°F (68°C)</td>
</tr>
<tr>
<td></td>
<td>Autoignition temperature</td>
<td>941°F (510°C)</td>
</tr>
<tr>
<td></td>
<td>Flammable limits in air:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower limit</td>
<td>0.67 volume % at 185°F (85°C) and atmospheric pressure</td>
</tr>
<tr>
<td></td>
<td>Upper limit</td>
<td>6.1 volume % at 248°F (120°C) and atmospheric pressure</td>
</tr>
<tr>
<td>DVB-63</td>
<td>Flash point, tag closed cup</td>
<td>156°F (69°C)</td>
</tr>
<tr>
<td></td>
<td>Autoignition temperature</td>
<td>921°F (494°C)</td>
</tr>
<tr>
<td></td>
<td>Flammable limits in air:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower limit</td>
<td>0.64 volume % at 185°F (85°C) and atmospheric pressure</td>
</tr>
<tr>
<td></td>
<td>Upper limit</td>
<td>6.1 volume % at 248°F (120°C) and atmospheric pressure</td>
</tr>
<tr>
<td>DVB-HP</td>
<td>Flash point, tag closed cup</td>
<td>157°F (70°C)</td>
</tr>
<tr>
<td></td>
<td>Autoignition temperature</td>
<td>879°F (470°C)</td>
</tr>
<tr>
<td></td>
<td>Flammable limits in air:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower limit</td>
<td>0.69 volume % at 185°F (85°C) and atmospheric pressure</td>
</tr>
<tr>
<td></td>
<td>Upper limit</td>
<td>6.2 volume % at 248°F (120°C) and atmospheric pressure</td>
</tr>
</tbody>
</table>

*For other operating conditions, consult The Dow Chemical Company.*

### Safe Handling Practices

Safe handling of DVB requires consideration of hazards inherent to hydrocarbons.

### Flammability

DVB will burn. Exercise the same precautions against fire and explosion hazards that are commonly applied to other combustible and flammable liquids. The flammability properties of DVB are given in the table above.

### Fires

Fires involving DVB can be safely extinguished with foam, dry chemical, or carbon dioxide extinguishers. Water is not an effective extinguishing agent for use on these water-insoluble monomers.

When burning, DVB can give off toxic by-products such as carbon monoxide gas. Wear approved respiratory equipment to avoid breathing any fumes or smoke.
Spills

Spilled monomer can be removed safely for disposal by covering it with a suitable adsorbing agent such as sand or ground corn cobs. However, some adsorbing agents such as untreated clays and micas may cause an exothermic reaction which might ignite the monomer. To be absolutely safe, adsorbing agents should be tested for their effect on polymerization of the monomer before they are used on 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.

If the spill is contained by a permeable barrier (such as with an earthen dam), you should 1) limit the area of exposure, 2) get water under the spill (DVB floats on water so this will prevent the monomer from soaking into the ground and allow it to be skimmed and pumped off later), and 3) put fire-fighting foam over the spill to control odor and prevent fire.

Use of a non-permeable barrier, such as a concrete dike, is recommended. If the spill is contained in such a non-permeable barrier, the use of water is not necessary and may be detrimental. Dikes around tanks are commonly sized to hold the contents of the tank and the addition of water may cause the dike to overflow.

Disposal

Incorporate the collected monomer in a properly designated furnace. Comply with federal, state, and local regulations. Call The Dow Chemical Company for additional recommendations.

Static electricity

DVB, with its high-volume resistivity, can pick up and hold a static charge during transfer from a tank truck to a storage tank. Always make sure that the storage tank and tank truck are well-grounded.

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

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

Distribution Emergency Response

Distribution Emergency Response (E/R) is the Dow system for advising and assisting anyone confronted with an emergency which occurs in the distribution of Dow products. E/R, a part of Dow’s commitment to Product Stewardship, can provide essential help to protect human health and environmental quality in chemical emergencies.


Or call CHEMTREC (day or night)
Toll-free 1-800-424-9300 (U.S.A., except Washington, D.C.)
1-202-483-7616 (Washington, D.C., and outside U.S.A.)
Extensive experience has shown that divinylbenzene can be handled safely if its toxicological properties are clearly understood and proper precautions are practiced.

Material Safety Data Sheets for divinylbenzene are available from Dow to help customers meet their own safe handling and disposal needs. Request and study this information before working with the monomer.

A brief summary of basic safe handling precautions for this monomer follows. The precautions recommended are, of necessity, general in nature, because specific recommendations can be made only when the actual conditions are known.

**Inhalation**

Inhalation of DVB can cause respiratory irritation and, at higher concentrations, anesthetic and narcotic effects. The ACGIH (American Conference of Governmental and Industrial Hygienists) Threshold Limit Value/Time Weighted average concentration (TLV/TWA) and the OSHA permissible exposure limit (PEL) for DVB are 10 ppm.

Vapor concentrations should be maintained below these guidelines. In the absence of proper environmental control, wear an approved, organic vapor-type respirator. In emergencies and other conditions where the guidelines are greatly exceeded, wear a positive-pressure, self-contained breathing apparatus.

Applications which require heating of DVB increase the likelihood of attaining hazardous vapor conditions. Exercise additional caution when working with DVB at elevated temperatures.

If a person is accidentally overcome by monomer vapors, or experiences any ill effects caused by breathing the vapors of these materials, move him/her immediately to fresh air, and keep him/her quiet and warm. Obtain medical attention immediately. If breathing stops, administer artificial respiration.
Skin contact

Brief skin contact with DVB (five minutes or less) usually causes no irritation. However, prolonged contact may cause irritation and possibly some swelling of the skin or even a burn, depending upon the severity of the exposure. Blistering of the skin can occur when clothing or shoes wet with DVB are worn, and skin rashes may result from repeated exposure.

Wear clean, body-covering clothing and Neoprene rubber gloves if hand contact is likely.

If skin contact occurs, wash the affected area immediately with plenty of water. Never use solvents to remove monomer from skin. Any injuries or irritation should receive prompt medical attention.

Eye contact

DVB is irritating to the eyes. Contact will be quite painful and can cause irritation of the conjunctival membranes that shield the eyes.

Wear safety glasses as minimum eye protection for divinylbenzene. If the eyes are contaminated, flush immediately for 15 minutes with plenty of water, and obtain medical attention as quickly as possible.

Ingestion

DVB is low in acute oral toxicity. Although DVB should never be ingested, if it is accidentally swallowed, DO NOT INDUCE VOMITING, because there is the danger that upcoming stomach fluids may be aspirated into the lungs, causing systemic effects. Medical attention should be obtained immediately.

NOTE TO PHYSICIAN: Because rapid absorption may occur through the lungs if aspirated, causing systemic effects, the decision of whether or not to induce vomiting should be made by an attending physician. If lavage is performed, endotracheal and/or esophageal control is suggested. Danger of lung aspiration must be weighed against toxicity when considering emptying the stomach. If skin burns are present, treat as any thermal burn after decontamination.
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   Washington, D.C., USA
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   Nitto Electric Industrial Co., Ltd.
   Japan
   Jpn. Kokai Tokkyo Koho JP 60/202731 A2
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   Tokuyama Soda Co., Ltd.
   Japan
   Jpn. Kokai Tokkyo Koho JP 58/67445 A2
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   Tokuyama Soda Co., Ltd.
   Japan
   Jpn. Kokai Tokkyo Koho JP 58/67445 A2
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   (to Sumitomo Chemical Company, Ltd.),
6. Adhesive Composition, George W. Feeney
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1. Biologically Active Reagents Prepared from Carboxy-Containing Polymer, Analytical Element
   and Methods of Use, Richard C. Sutton
2. Sensor Devices, Michael G. Clark
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   Nephelometry Test Samples, James A. Patterson
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   AKZO N. V. Neth.
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   Heller, Harold; Schaepel, Dietmar; Hentschel, Claus; Dahm, Manfred
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4. Resin-Linker Combination for the Solid-Phase Synthesis of Peptides and Intermediates, Monika Mergler, (to Bachem Feinchemikalein A.G.),

5. Synthetic Polystyrene Resin and its Use in Solid Phase Peptide Synthesis, Hans Rink, (to Ciba-Geigy Corporation),


9. Lewis Acid-Catalyzed Polymerization of Biological Oils and Resulting Polymeric Materials, Richard C. Larock, (to Iowa State University Research Foundation, Inc.),

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11. Surface-M Modified Polymer Beads, Robert M. Strom, (to The Dow Chemical Company),

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1. Hydrogen-water exchange catalyst
   Nakane, Ryohei; Isomura, Shohei; Morishita, Teizo; Noda, Shigeyuki
   Institute of Physical and Chemical Research; Hikari Kogyo Co., Ltd.
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   Texaco Inc.
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Res. Div., Bridgestone Tire Co., Ltd.
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