DuPont™ Hytrel® Handling and Processing Precautions

THERMOPLASTIC POLYESTER ELASTOMER

DUPONT®

The miracles of science™

Introduction

This guide provides an overview of the available physical and toxicological hazard information when handling or processing DuPont™ Hytrel® thermoplastic polyester elastomers. In addition to the general purpose molding and extrusion grades of Hytrel®, information is also included on the additive-containing concentrates.

The information contained in this product handling guide is offered only as guidance. Users must determine to their own satisfaction if operating procedures, processes, and additives are compatible with Hytrel® resins, comply with applicable governmental regulations and provide a safe working environment for employees and customers. Additional Safety Information can be found in the appropriate "Material Safety Data Sheet" (MSDS) for each product. For a current MSDS on Hytrel®, call 1-800-441-0575 (select Engineering Polymers when prompted) (U.S.).

1-800-387-2122 (Canada)

+41-22-717-5111 (Europe 08:00 – 18:00 CET)

1-302-774-1000 (all others)

General

Hytrel® thermoplastic polyester elastomers, as polymer powders or pellets, are considered to be of low acute toxicity. Uncompounded Hytrel® thermoplastic polyester elastomer resins are generally not skin irritants or sensitizers. However, some grades, because of the type of additive selected, may be irritating to the skin.

Certain compounded Hytrel® grades contain various additives, mainly to impart heat and ultraviolet light stability. When Hytrel® resins are heat processed (particularly compounded grades containing flame retardant (FR)-, moisture- or heat stabilizer-packages, several potentially hazardous thermal decomposition products may be emitted from the resin. As noted in the section on ventilation, use of local exhaust and general ventilation is essential in processing areas to keep concentrations of volatile thermal decomposition products below workplace exposure limits.

Health Hazards — Toxicity

The acutely lethal ingested dose (ALD) in male rats for an uncompounded Hytrel® was determined to be greater than 25,000 milligrams per kilogram of body weight, indicating low acute toxicity. Other grades of uncompounded Hytrel® have similar chemistry and are expected to have the same low order of acute oral toxicity.

Dust (Fines)

Dust may be generated by operations such as grinding. As with any dust, an appropriate respirator should be worn if dusts are generated and exposures are (or are expected to be) above workplace control limits.

Uncompounded grades of Hytrel® sold in powdered form are considered to be of a low acute toxicity by inhalation. Within DuPont, the workplace control limits for Hytrel® dusts in air are 10 milligrams per cubic meter maximum for total dust and 5 milligrams per cubic meter maximum for respirable dust (defined as <3 µm aerodynamic equivalent diameter). The OSHA Permissible Exposure Limit for respirable particles not otherwise regulated is 5 mg/m^3. If exposures above this limit are anticipated, use a NIOSH-approved respirator.

Hytrel® grades compounded with FR additives, 51FR and 52FR are compounded products containing a flame retardant based on a bromine-containing compound plus antimony trioxide. Inhalation of antimony trioxide particles has caused lung cancers in laboratory animals (IARC considers antimony trioxide to be a possible human carcinogen). However, since the additives compounded in these Hytrel® resins are encapsulated in a high-molecular-weight polymer, exposure to the component flame retardant chemicals via inhalation of dust is not normally a problem. Nonetheless, workplace exposure to antimony oxide (fumes or dust) must be kept below 0.5 milligrams per cubic meter (as antimony, OSHA Permissible Exposure Limit).

Physical Hazards — Spills

Spills of any process material may pose a slipping hazard. Spilled pellets and powders should be swept up immediately and disposed of properly.

Precautions During Processing

Standard Operating Conditions

There are two hazards to guard against during routine processing: burns and emission of thermal degradation products, primarily gases/vapors. Also, prolonged or repeated skin contact should be avoided when processing certain compounded grades containing irritant or sensitizing additives (such as Hytrel® 10MS or other grades containing polycarbodiimide). Minimize skin contact whenever possible by wearing appropriate protective gloves.

Burns

Painful and serious thermal burns can result from skin contact with molten polymer at normal processing temperatures of 175 to 260°C (347 to 500°F). Wear heat resistant gloves and long sleeved attire with the cuffs buttoned when exposure to molten polymer is likely. If molten Hytrel® comes into contact with skin, immediately cool the polymer and burned areas of skin by immersion in cold water or with ice to minimize burn injury. Do not forcibly remove the polymer which may also remove skin. Call a physician.

Thermal Degradation of DuPont™ Hytrel®

Polymer Decomposition Products

Hytrel® thermoplastic polyester elastomers can degrade in an extruder or molding machine, forming volatile decomposition products. These products can be hazardous to breathe and cause blow-back or fire.

The composition and concentration of Hytrel® degradation products is a function of the specific additives, the processing temperature and the time at that temperature. Specific processing temperatures are suggested in individual Hytrel® product data sheets.

Thermal decomposition of Hytrel® may evolve primarily tetrahydrofuran (THF; arising from a monomer used in polymerization) with lesser amounts of various oxidation products (listed in decreasing relative amounts): carbon dioxide, carbon monoxide, acetic or formic acids, isobutylene, mixed aldehydes (acetaldehyde, propionaldehyde, acrolein), and/or other low molecular weight oxygenated species. Available OSHA recommended Permissible Exposure Limits for these substances is shown in **Table 1**. THF, the major decomposition product, may evolve at a temperature slightly above the melting point of the polymer. THF is a potential fire or explosion hazard (open cup flash point –14°C [6°F]) and caused cancer in rodents by chronic inhalation. Formation of THF vapors can also occur under any of the conditions mentioned in the "Polymer Decomposition Products" section.

Depending upon the compounding additives incorporated into some Hytrel® resins, other decomposition products may be emitted upon heating. These emissions are discussed in the section on "Concentrates".

Ventilation During Polymer Processing

Melt processing of thermoplastic resins (e.g., extrusion, blow molding, injection molding) will release volatile decomposition products that may be harmful to your health or create undesirable odors. The most effective way to control these emissions is to "capture" them at the point of release and remove them by exhaust ventilation before they are dispersed into the air you may breathe. This "capture" technique is called local exhaust ventilation (LEV). LEV (such as exhaust ducts/hoods placed at the source of emission) is highly effective and should be the primary engineering control for processing emissions; general room ventilation, is also important but not as effective as LEV in preventing accumulation of thermal decomposition product emissions in the workplace. Proper design and operation of the ventilation system is important to insure collection and extraction of processing fumes from the work spaces. Hood design and calculation of minimal functional air velocity is best performed by knowledgeable design engineers.

Table 1
Some Workplace Control Limits for the Thermal Decomposition Products from DuPont™ Hytrel® Thermoplastic Polyester Elastomers[1]

Compound	PEL (ppm)[2]	TLV (ppm)[3]	STEL (ppm)[4]
Tetrahydrofuran	200	50	100
Carbon dioxide	5000	5000	30000
Carbon monoxide	50	25	200
Isobutylene	NA	NA	NA
Acids			
Acetic	10	10	15
Formic	5	5	10
Aldehydes			
Acetaldehyde	200	NA	25 (Ceiling)
Propionaldehyde	NA	20	NA
Acrolein	0.1	NA	0.1 (Ceiling)
Butyrolactone	NA	NA	NA
Dihydrofuran	NA	NA	NA
t-Butanol	100	100	150

[1] Listed in relative abundance based on isothermal gas chromatography/mass spectroscopic analysis of two different Hytrel® grades at approximately 200°C. Compositional data are for information purposes only and may not reflect actual composition or concentrations of hazardous gases presented by these materials under actual processing conditions.
[2] Permissible Exposure Limit (PEL) for 8 hours exposure as developed by the US Occupational Health and Safety Administration (OSHA).
[3] Threshold Limit Value (TLV) for 8 hr as reported by the American Conference of Governmental Industrial Hygienists (2007).
[4] Short Term Exposure Limit (STEL) for 15 minutes as reported by NIOSH (National Institute for Occupational Safety and Health) or the American Conference of Governmental Industrial Hygienists (2007), whichever was lower.

Visual observation or reliance upon odor detection should not be used to determine the effectiveness of any ventilation system. While worker discomfort from odors is usually a sign that ventilation problems exist, it should be noted that for some substances the exposure limit can be below the concentration at which its odor can be detected.

When processing plastic resins at elevated temperatures, it is very important that adequate ventilation be provided and its effectiveness checked by measurement of emission product concentrations in the work area.

References include:

American National Standards Institute standard Z9.2-1979, "Fundamentals Governing the Design and Operation of Local Exhaust Systems."

DuPont Engineering Polymers "Proper Use of Local Exhaust Ventilation during Processing of Plastics", available from Customer Service (1-800-441-0575) or www.plastics.dupont.com

Polymer Decomposition

DuPont™ Hytrel® thermoplastic polyester elastomers can decompose under the following conditions:

- excessively high temperature in the barrel;
- moisture level above 0.1 percent;
- localized holdup within the extruder/molding machine;
- molten polymer held in the machine too long at normal operating temperatures; or
- additives or contaminants that promote decomposition at normal operating temperatures.

Danger signals warning that the polymer is beginning to degrade and decompose are frothing and/or spitting of molten polymer at the nozzle or die, pronounced odor, discolored polymer, or badly splayed parts.

If decomposition occurs, heat should be shut off and the machine should be purged. Medium viscosity, low density polyethylene resin is recommended for purging. (Some common thermoplastic resins are unstable or do not melt at the temperature required for purging Hytrel® thermoplastic polyester elastomers and are not recommended). Usually, high pressures will not result from decomposition unless a cold plug is formed in the die or adaptor section of an extruder, or unless the ram of a molding machine is advanced so that the gas cannot escape through the feed port. Accordingly, when molding or extruding Hytrel®, it is important that the operator be familiar with the factors which can cause decomposition, danger signals which warn of this problem, and the actions that must be taken to prevent pressure buildup and possibly hazardous consequences such as "blow-back", rupture of molding equipment or fire.

Maximum Processing Temperature

The maximum suggested melt processing temperature for most grades of Hytrel® thermoplastic polyester elastomers is 270°C (520°F). However, note that the maximum melt processing temperatures are lower for the following grades:

- HTR8068 is 210°C (410°F)
- HTR8105BK is 250°C (480°F)
- HTR8136BK is 250°C (480°F)
- HTR8139BK is 250°C (480°F)

Potentially hazardous gases can also occur in post-processing operations. Examples are hot-wire cutting and heat sealing of films of Hytrel®, where polymer adhering to the hot wire or sealing bar can pyrolyze, emitting potentially hazardous polymer decomposition products. As noted above, proper use of LEV limits emissions of these volatile substances in processing or work areas.

"Blow-Back"

The gases generated during decomposition can create high pressures if confined. If molten material is not free to exit from an injection cylinder through the nozzle, it may "blow-back" through the hopper; likewise, if the die of an extruder is plugged, sufficient pressure may be generated to warp or rupture the adaptor and die system. Pressure buildup can be high and rapid, and metal parts could rupture suddenly with possible injury to personnel.

Fire

Hytrel® thermoplastic polyester elastomers can ignite and burn if exposed to temperatures above the normal processing range. Danger of fire through ignition of THF or other flammable vapors, resulting from the decomposition of Hytrel® resins, can be minimized by providing good ventilation in the processing area.

Generation of THF vapor may be minimized by dropping overheated Hytrel® resins into water.

Combustion is a complex process dependent upon several factors, including: actual temperatures, access of air and removal of gaseous products. Interactions may occur under particular combustion conditions to give different products. Combustion products from Hytrel® base resins can vary depending upon the conditions and additives present but may contain THF, carbon dioxide, carbon monoxide, and similar products (oxidized low molecular weight hydrocarbons such as organic acids and aldehydes) as those identified in the preceding section on "Polymer Decomposition Products". Other possible thermal decomposition products are described in the "Concentrates" section and are listed on individual MSDS.

Precautions During Molding

Ovens should be safely vented and molded items should not be cut open until cooled, and even then only with adequate ventilation. The presence of irritating fumes (probably acrolein) has been noted upon cutting open a hot roto-molded tank, but fumes were not observed if the part was allowed to cool before slitting.

Given the elevated temperatures used in rotational molding, increased thermal decomposition and emission of volatile byproducts (such as those described in the "Polymer Decomposition Products" section) are more likely to occur. For this reason, it is important that each rotational molding operation be evaluated for proper ventilation and provided with a fresh air supply. LEV should be used to keep irritating fumes out of the work area. If there is doubt about adequate ventilation, then air monitoring for the substances shown in **Table 1** is recommended.

Due to either their physical properties or potential to generate hazardous offgases, it is recommended that the following grades of DuPont™ Hytrel® thermoplastic polyester elastomers not be rotomolded: HTR8068, HTR8136BK, HTR8105BK, HTR8139LV, and any compound containing the concentrates Hytrel® 51FR , 52FR or Hytrel® 10MS.

Precautions Relating to Compounding

Materials with a pH of less than 7, such as acidic clays with pH 4.5 to 5.5, can promote decomposition of Hytrel® thermoplastic polyester elastomers. **Therefore, compounding of Hytrel® with acidic pigments, lubricants, or additives should be avoided.** Other compounding ingredients or additives used to make end products may present other hazards in handling and use. Before proceeding with any compounding or processing work, consult and follow label directions and handling precautions from suppliers of all ingredients.

Concentrates

In the United States, DuPont offers five additive-containing concentrates, Hytrel® 10MS, Hytrel® 21UV, Hytrel® 30HS, Hytrel® 40CB, Hytrel® 51FR and 52FR . Each concentrate is designed to be blended with other Hytrel® resins to enhance specific properties. Normally recommended letdown ratios for blending of the concentrates with unmodified Hytrel® are as follows:

Hytrel® 10MS-10 to 1 (10 parts of Hytrel® to 1 part of concentrate)

Hytrel® 21UV - 40 to 1[1]
Hytrel® 30HS - 20 to 1
Hytrel® 40CB - 16 to 1[2]
Hytrel® 51FR, 52FR - 10 to 1

[1] For best outdoor service life a 25 to 1 letdown is recommended.

[2] For best outdoor service life a 7 to 1 letdown is recommended.

All of these concentrates are dispersed in a Hytrel® carrier resin. As such, all concentrates should be handled with at least the same precautions and ventilation needs as the regular unmodified types of Hytrel® resins.

Even though the concentrates are normally used in low concentrations as indicated above, five of the concentrates, Hytrel® 10MS, Hytrel® 21UV, Hytrel® 30HS, and Hytrel® 51FR and 52FR, may liberate additional thermal decomposition products from those listed in the "Polymer Decomposition Products" section during processing. As noted previously, use of LEV is essential to remove any irritating substances from the processing and work areas. The concentrates are reviewed individually in the following section.

Hytrel® 10MS Hydrolytic Stabilizer Concentrate

Hytrel® 10MS is a concentrate of polycarbodiimide (PCD), a hydrolysis stabilizer, in a 40D grade of Hytrel® thermoplastic polyester elastomer. It contains 20 percent PCD by weight. An additive in Hytrel® 10MS can decompose at lower temperatures than those typically used in molding Hytrel® resins and may evolve substituted aromatic isocyanates or amines (which are irritating to breathe and possible skin/respiratory sensitizers), THF and acrolein when heated. Heating mixtures of Hytrel® 10MS with other Hytrel® grades could also generate these products.

Substituted aromatic isocyanates, such as 2,6-diisopropyl phenyl isocyanate (DIPPI) or 2,4,6-triisopropyl phenyl diisocyanate (TRIDI) and corresponding amines may be formed above the decomposition temperature of the PCD (approximately 180°C). Exposure limits for these particular aromatic isocyanates/amines are not known. The workplace exposure limits for a related isocyanate, toluene diisocyanate (TDI) is 20 ppb (0.16 mg/m^3) according to OSHA but the American Conference of Governmental Industrial Hygienists (ACGIH) TLV limit as an 8-hr TWA is 1 ppb (0.008 mg/m^3) with a 3 ppb ceiling (15 min Short Term Exposure Limit [STEL]). Exposure to these substances above regulated limits can be harmful, resulting in difficult and labored breathing, or asthma. Acrolein may cause tearing, and eye, nose, and throat irritation. Acrolein is regulated as an air contaminant in the United States by OSHA (see Reference D) with a Permissible Exposure Limit (PEL) of 0.1 ppm (0.25 mg/m^3).

Products containing Hytrel® 10MS or polycarbodiimide may cause skin irritation and/or skin/respiratory sensitization. Minimize skin contact whenever possible by wearing appropriate protective gloves.

DuPont™ Hytrel® 21UV Ultraviolet Light Stabilizer

Hytrel® 21UV is a concentrate of HALS and ultraviolet light stabilizers in 40D Hytrel®. No toxicity data exists for Hytrel® 21UV; reported effects in rats from repeated exposure to the individual additives in Hytrel® 21UV include liver, kidney or spleen damage, and blood or immune system effects. Thermal processing of Hytrel® 21UV is not expected to generate volatile emission products that differ in composition from that of Hytrel® base resin. If likely to be exposed to dusts from grinding or machining operations above the recommended limits, wear a NIOSH approved respirator. Again, use of LEV is essential to remove any irritating substances from the processing and work areas. Pellets of Hytrel® 21UV may cause skin irritation.

Hytrel® 30HS Heat Stabilizer

Hytrel® 30HS is a concentrate of antioxidants in 40D Hytrel®. Volatile thermal decomposition products from heating Hytrel® 30HS have not been experimentally determined but are expected to be similar to Hytrel® base resin, and may also include caprolactam (TWA 5 ppm), ammonia, oxides of nitrogen and traces of hydrogen cyanide.

Hytrel® 40CB Carbon Black Concentrate

Hytrel® 40CB contains carbon black dispersed within 40D Hytrel®. Carbon black has produced lung tumors in rats by a mechanism not believed to apply to humans. Since the carbon black compounded in this grade is encapsulated in a high-molecular-weight polymer, exposure to the carbon black component via inhalation of dust is not normally a problem. Handling precautions for this product should be the same as for non-modified Hytrel® thermoplastic polyester elastomer.

Hytrel® 51FR and 52 FR Flame Retardant Concentrates

Hytrel® 51FR and 52FR are concentrates containing 67 percent by weight of a bromine-containing additive plus antimony trioxide, dispersed in 40D and 55D Hytrel®, respectively. The brominated flame retardant was not irritating to skin or eyes, has low acute or repeated dose toxicity, and was neither a developmental toxicant nor a mutagen.

The brominated flame retardant used in Hytrel® 51FR and 52FR has a decomposition temperature in excess of 300°C (572°F). During heating of Hytrel® 51FR and 52FR, fumes irritating to the eyes and mucous membranes of nearby personnel may be released. Thermal decomposition product analysis from heating flame retardant Hytrel® grades has not been conducted but decomposition products, in addition to those previously described for Hytrel® base resin, may include HBr (an upper respiratory tract irritant; with an OSHA PEL of 3 ppm and ACGIH TLV of 2 ppm ceiling), hydrogen cyanide (an asphyxiant; OSHA PEL of 10 ppm and ACGIH TLV of 4.7 ppm) and oxides of nitrogen. Do not mix Hytrel® 51FR and 52FR with either Hytrel®10MS or Hytrel® 21UV; blends of these may rapidly decompose, liberating potentially hazardous emissions.

Some operations such as machining may produce dust from Hytrel® 51FR and 52FR. Inhalation of dust should be avoided; a NIOSH-approved respirator should be used if exposure to dusts above recommended limits (see section on Dusts) is anticipated. Antimony trioxide (Sb_20_3), acts as a synergist in the flame retardant, and although not highly toxic by acute inhalation, it produced lung cancer in laboratory animals. To protect against possible health hazards of antimony, occupational exposure to (Sb_20_3) dust (measured as antimony) should be kept below 0.5 mg/m^3 (OSHA and ACGIH TLV limits); within DuPont, the occupational control limit (8-hr TWA) for (Sb_20_3) is 0.2 mg/m^3, as antimony.

Waste Product Disposal

Preferred options for waste disposal are (1) recycling, (2) incineration with energy recovery, and (3) landfill. Landfill can be used for all Hytrel® thermoplastic polyester elastomer grades including Hytrel® 51FR and 52FR and HTR8068, providing the method is in compliance with federal, state and local regulations.

The high fuel value of this product makes option (2) very desirable for products that can't be recycled. Forced draft incineration is the alternate method for disposal of all types of Hytrel® except Hytrel® 8068 and Hytrel® 51FR and 52FR (see Concentrates, page 5). Under good combustion conditions, such as found in forced draft incinerators, Hytrel® thermoplastic polyester elastomers are converted to carbon dioxide, water, and trace components. These combustion products are not known to pose health hazards. The incineration method must be in compliance with local, state and federal regulations.

Incomplete combustion of Hytrel® thermoplastic polyester elastomers may emit volatile decomposition products similar to those shown in **Table 1**. Carbon monoxide, THF, mixed aldehydes (acrolein, acetaldehyde and propionaldehyde), and organic acids may be the most hazardous components produced by incomplete combustion. For this reason, combustion

of waste DuPont™ Hytrel® is not recommended unless the oxygen supply can be maintained in amounts adequate for full combustion. With open burning, dump fires, and pit burning, combustion is usually not complete, so these methods should not be used to burn waste Hytrel®. Smoke produced under limited oxygen supply conditions should be considered toxic and should not be inhaled, as is true for smoke produced from wood or paper burned under poor combustion conditions.

Environmental Testing

Hytrel® is classified as a non-hazardous waste as codified in 40 CFR Section 261.2 of the US EPA regulation and determined by the Toxicity Characteristic Leaching Procedure found in 40 CFR Section 261.24. If Hytrel® is modified, such as addition of a pigment containing heavy metals, it is the responsibility of the generator of the solid waste to determine if it is subject to the regulation and compliance with applicable requirements for disposal.

References

A. 2007 TLV and BEIs. Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Reprints available from ACGIH, 1330 Kemper Meadow Drive, Cincinnati, OH 45240-3355.

B. Code 29 CFR 1910.1000.

For information on Engineering Polymers contact our regional headquarters or visit us on the web at plastics.dupont.com for the complete listing of our offices around the globe.

Europe, Middle East & Africa
DuPont de Nemours International S.A.
Geneva, Switzerland
Customer Information Center
Toll-free +800 3 876-6838
Tel: +41 22 717-5950
Fax: +41 22 717-5948
E-mail us at: eu-info@dupont.com

North America
DuPont Engineering Polymers
Wilmington, Delaware, USA
Toll Free: (800) 441-0575
Tel: (302) 992-4592
Telefax: (302) 992-6713
E-mail us at: Web-inquiries.DDF@usa.dupont.com

South America
DuPont do Brasil S.A.
Al. Itapecuru, 506 Alphaville
06454-080 Barueri-Sao Paulo
Tel: (5511) 4166-8299
Fax: (5511) 4166-8513

Asia Pacific
DuPont Kabushiki Kaisha
Sanno Park Tower, 11-1
Nagata-cho 2-chome
Chiyoda-ku, Tokyo 100-6111
Japan
Tel: (81-3) 5521 8500
Fax: (81-3) 5521 2595

DuPont China Holding Co. Ltd.
Shanghai Branch
399 Keyuan Road, Bldg. 11,
Zhangjiang Hi-Tech Park,
Pudong New District, Shanghai,
P.R. China (Postcode: 201203)
Tel: 86-21-3862-2888
Fax: 86-21-3862-2889

K-16844 (01/08) Printed in the U.S.A.

DUPONT®

The miracles of science™