



DuPont™ Vamac®

Safe Handling and Processing of Vamac® and Compounds made from Vamac®

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Read and understand the Material Safety Data Sheet (M/SDS) before using DuPont™ Vamac® ethylene acrylic elastomers.

Toxicity Information Related to the Handling and Processing of Vamac®

Vamac® ethylene acrylic elastomers are made from ethylene, methyl acrylate and a cure site monomer. Normally, they are blended with typical rubber ingredients and then processed and cured. There are many different compounds made from Vamac® elastomers, and they use various mixing and processing conditions and curing processes. This literature reviews the safe handling of Vamac® elastomers and gives a general overview of handling compounds based on Vamac® elastomers.

Vamac® Polymer and Methyl Acrylate Monomer

Vamac® elastomers or polymers fall into two general categories. The majority of them are terpolymers made from ethylene, methyl acrylate and a cure site monomer. These terpolymers are normally cured with diamines. The other category of Vamac® polymers is dipolymers which are made from ethylene and methyl acrylate. Dipolymers are normally cured with organic peroxides.

All Vamac® elastomers contain some residual methyl acrylate monomer (CAS number 96-33-3). A typical level of residual methyl acrylate monomer is 0.15% by weight (1500 ppm). Most of this monomer is lost during the processing and curing steps and very little is found in the finished parts. Methyl acrylate exposure in the workplace where Vamac® elastomers are processed can be controlled within the desired limits by the use of proper ventilation (for example local exhaust ventilation).

High vapor concentrations can cause irritation to eyes, nose, throat and lungs. Overexposure can lead to pulmonary edema and possible injury to liver and kidneys. Methyl acrylate can be absorbed through the skin.

Methyl acrylate is regulated as an air contaminant in the United States under the Occupational Safety and Health Act per 29 CFR 1910.1000 Air Contaminants, with an 8-hour time weighted average (TWA) permissible exposure limit (PEL) of 10 ppm (skin)*.

The American Conference of Governmental Industrial Hygienists (2011 edition) sets an 8-hour TWA threshold limit value (TLV) of 2 ppm (skin). DuPont has established a 15-minute TWA of 5 ppm (skin) as an acceptable exposure limit (AEL). DuPont applies this limit to its manufacturing and laboratory operations for Vamac®.

Other regions of the world may have different allowable occupational airborne levels of methyl acrylate monomer. Please consult the local regulations.

*A skin notation indicates that dermal exposure can be a significant contributor to the overall exposure (i.e., in addition to inhalation exposure) and subsequent internal doses in the body.



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The odor threshold for methyl acrylate is approximately 14 parts per billion (ppb). Therefore, sense of smell is not a reliable indicator of the methyl acrylate airborne concentration in an area. Repeated exposure can desensitize the nose.

Adequate control of exposure to methyl acrylate and other decomposition products from processing can be realized by proper ventilation. The ventilation requirements of each plant location and operation may differ sufficiently to warrant individual methyl acrylate monitoring of each area. Areas where DuPont™ Vamac® is stored should be assessed as well as the processing areas. Actual concentration of methyl acrylate in air can be determined by using a gas analyzer.

The DuPont brochure on “Proper Use of Ventilation During Processing of Plastics” has some good suggestions on how to limit worker exposure to air borne chemicals. Please contact your local DuPont representative if you would like a copy.

Compounds made from Vamac® – Handling Precautions while Processing

There are many possible steps used to process compounds made from Vamac® including mixing, molding, de-molding, extrusion, curing, post curing, etc. During the processing steps, some gaseous byproducts will be vaporized into the air in the immediate work area. The composition of these vapors will depend on the compounding ingredients added to the compound along with the process conditions such as temperature and pressure. Many of the rubber compounding ingredients have a substantial vapor pressure at elevated temperatures and can contribute significantly to the amount of volatiles. Therefore, only general guidelines for handling precautions can be provided.

As mentioned previously, most of the Vamac® polymers used today are based on terpolymers (i.e. Vamac® G and Vamac® GLS) and these are cured with diamines. The following discussion relates to terpolymers. Dipolymers are cured with peroxides and will have different volatiles.

A typical compound made from a Vamac® terpolymer may have a formulation that has the ranges listed below:

- 100 parts polymer
- 50 to 80 parts carbon black
- 0 to 20 parts of a plasticizer
- 1 to 3 parts of a release package
- 1 to 3 parts of an anti-oxidant
- 1 to 2 parts of a curative – usually hexamethylene diamine carbamate (HMDC)
- 1 to 5 parts of an accelerator – diorthotolyl guanidine (DOTG) or Diazobicyclo undecene (DBU)

The compound will usually be mixed on an internal mixer at about 100 °C (212 °F) and then sheeted off on a roll mill. It will then either be extruded into a hose or molded. Typical process temperatures for extruding hoses are about 60 to 90°C (140 to 194°F). For molding, the temperature can be around 180°C (356°F). For most of the molding cycle the mold is closed and under pressure (limited volatiles) but at the end of the molding cycle the mold is open to atmospheric pressure and this is when the volatiles concentration will be the highest.

In the final processing step a hose will be cured in an autoclave at about 175 °C (347 °F) under pressure. Molded parts are usually post cured for several hours at about 175 °C (347 °F) at ambient pressure.

During the curing step the HMDC curative will break down to hexamethylene diamine (HMDA) and carbon dioxide (CO₂). Also during the cure step the diamine/cure site reaction will generate water and ethanol. The weight loss from these volatiles for a compound with 1.5 phr of HMDC and a total of 200 parts will be:

- 0.21% weight loss from CO₂ produced when HMDC is converted to HMDA
- 0.17% weight loss from water generated during cure
- 0.43% weight loss from ethanol generated during cure

The total volatiles from the cure system (CO₂, water and ethanol) are about 0.8% by weight for a typical compound.

The amount and nature of the other volatiles encountered during the vulcanization of an elastomer are difficult to assess since chemical side reactions can take place. These reactions and the volatiles

generated depend on the specific compound formulations and the type of curing system. The concentration of volatiles in a given area will depend on many factors including the length of the heating cycle, the size of the part, the access to the atmosphere, the size of the area and the degree of air circulation.

The off-gases generated in the curing of a typical compound made from a Vamac[®] terpolymer are shown in *Table 1*. These values are shown for information only and should not be used to predict concentrations of off-gases in a given work area. If there are any questions, it is suggested that processors of compounds made from Vamac[®] monitor for possible off-gases and measure the actual concentrations in the workplace.

**Table 1 – Off-Gases Generated During Isothermal Heating – 20 minutes at 177 °C
Off-Gas Concentrations are Given in Weight Percent of Compound**

Ingredient	PHR	Function
Vamac [®] G	100	Terpolymer
Vanfre [®] VAM	1	Release agent
Armeen [®] 18D	0.5	Release agent
Stearic Acid	2	Release agent
Naugard [®] 445	2	Anti-oxidant
N-550 Black	70	Carbon black
Nycoflex [®] ADB 30	20	Plasticizer
DOTG	4	Accelerator
Diak [™] #1 (HMDC)	1.5	Curative
Total phr	201	
Off-Gas Concentrations		Wt. Percent
Ethanol		0.1940
Acetone		0.0004
t-Butanol		0.0022
Benzene		0.0005
Aniline		0.0014
alpha Methyl Styrene		0.0081
o-Toluidine		0.0860

The allowable employee exposure level for these chemicals is different in the various regions throughout the world. **Please consult local regulations in order to ensure compliance.**

Ortho-Toluidine (O-Toluidine)

There are two possible sources of O-Toluidine for a compound that uses the accelerator DOTG. The O-Toluidine may be present at low levels in the DOTG itself. The O-Toluidine is also a decomposition product from the DOTG at temperatures typically used in the molding presses and post cure ovens.

O-Toluidine (CAS 95-53-4) is classified as carcinogen by IARC, NTP, OSHA and ACGIH. Please consult the MSDS for DOTG and O-Toluidine to ensure proper handling of these materials.

A qualitative study was run on a compound made from Vamac[®] that contained DOTG to observe O-Toluidine levels. Head Space-GC/MS (gas chromatography/mass spectroscopy) was run on samples after a simulated press cure (5 minutes at 177 °C) and after a simulated post cure (4 hours at 177 °C). Trace levels of O-Toluidine were measured after the press cure simulation and higher levels were observed after the post cure simulation.

A biological monitoring study was conducted on workers at two rubber plants in Germany and the study observed levels of O-Toluidine in the air as well as in blood and urine samples of the workers [“Aromatic Amines in the Rubber Industry – Biological Monitoring and Biochemical Monitoring”, T. Weiss, G. Korinth, H. Drexler, J. Angerer, 2005]. The study suggests that skin is the primary route of incorporation of O-Toluidine for accelerators (e.g. DOTG) that may release O-Toluidine. Customers and processors using

accelerators that may release O-Toluidine should evaluate the study and refer to industrial hygiene regulatory standards applicable to their workplace and consider whether additional precautions may be necessary to protect workers handling accelerators against overexposure via skin.

Some of the other accelerators used in compounds made from Vamac® are based on Diazobicyclo Undecene (DBU). A commercially available accelerator that uses DBU is Vulcofac® ACT 55. A compound containing Vulcofac® ACT 55 as the accelerator in place of the DOTG was included in the Headspace GC/MS study. No O-Toluidine was observed in the off gases from either the simulated press cure or simulated post cure steps.

Thermal Decomposition Products at Elevated Temperatures

If DuPont™ Vamac® polymers are subjected to abnormally high temperatures (about 316 °C or 600 °F and above), decomposition products derived from random cleavage and oxidation of the polymer can be obtained. Such temperatures can occur in a fire or during exposure to an unusual heat source. Some of the major decomposition products identified by gas chromatography – mass spectroscopy include: methanol, ethanol, acetone, dimethyl formal, ethyl acetate, the carboxylic acids: acrylic, propionic, methacrylic, butanoic, pentanoic, hexanoic, undecanoic and corresponding methyl esters.

Compounding Ingredients

For information and recommendations on the safe handling of curatives and other compounding ingredients used in formulations of Vamac®, contact the suppliers of those materials.

Waste Disposal

Material Safety Data Sheets (MSDS) describing proper waste disposal of DuPont materials are available on request.

Proprietary Materials

Sources of compounding ingredients mentioned in this bulletin are given below. Comparable materials from other suppliers may give equally satisfactory results.

Physical Form

Vamac® ethylene acrylic elastomers are supplied in the form of bales, wrapped in either EMA flexible wrap or PE strippable wrap. The clear flexible wrap need not be removed from the bale as it is intended to melt into the compound during mixing. The blue strippable wrap must be completely removed from the bale prior to processing to avoid potential contamination of the compound. It is important to ensure that no remaining fragments of blue strippable wrap remain adhered to or caught up in the folds of the polymer prior to mixing.

Material	Composition	Supplier
Vamac®	Ethylene/Acrylic Elastomer	DuPont Wilmington, DE
Diak™ No. 1	Hexamethylene Diamine Carbamate	DuPont Wilmington, DE
DOTG	Di-o-Tolyl Guanidine	Sovereign Chemical Akron, OH
Armeen® 18D	Octadecyl Amine	Akzo Nobel Chemicals Chicago, IL
Vanfre® VAM	Complex Organic Phosphate Ester Acid	R. T. Vanderbilt Co. Inc. Norwalk, CT
Naugard® 445	4,4-Bis-(,a,a'-Dimethylbenzyl) Diphenylamine	Chemtura Middlebury, CT
N-550	Carbon Black	Engineered Carbons Borger, TX
Nycoflex® ADB 30	Plasticizer	Safic-Alcan Paris, France
Vulcofac® ACT 55	Accelerator	Safic-Alcan Paris, France

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Caution: Do not use in medical applications involving permanent implantation in the human body. For other medical applications, discuss with your DuPont customer service representative and read Medical Caution Statement H-50103-3.

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