# Handbook of Foaming and Blowing Agents

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ChemTec Publishing

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# 1

# Introduction

Material foaming is one of the important processes, which generally lead to the lighter and more cost-effective materials, but frequently help to develop unique products for unique applications.

This field similar to many other technical fields makes use of terms which are sometimes not very well defined and therefore misused. Before addressing subject matter in a comprehensive way, it will be useful to review and define the most frequently used terms. They include:

- The foaming agent is a detergent which reduces surface tension, useful in converting a liquid to foam. The foaming agent (or surfactant) increases colloidal stability of foam, produced in its presence, by reducing the coalescence of bubbles. In another definition, a foaming agent is a material that facilitates the formation of foam such as a surfactant or a blowing agent. This differs from the previous definition because it includes two different groups of materials: surfactants and blowing agents considering that they both produce foams. The last definition seems reasonable, especially that the terms of foaming and blowing agents are frequently used interchangeably.
- The blowing agent, as defined by Wikipedia, is a substance which is capable of producing a cellular structure *via* a foaming process in a variety of materials that undergo hardening or phase transition, such as polymers, plastics, and metals. Chemical and physical blowing agents are distinguished. Chemical blowing agents are mixed into the plastics at lower temperatures. Then, above a certain temperature specific to each blowing agent, gaseous reaction products are evolved which help to produce foamed structure. Physical blowing agents are metered into the plastics, most frequently in the form of a melt, and they form bubbles by various means discussed in detail in Chapter 10. The blowing agents are further divided into endothermic and exothermic foaming agents. The endothermic chemical foaming agents are chemical compounds that take heat away from the chemical reaction. This produces foams with a much smaller cell structure, resulting in improved appearance and better physical properties. The exothermic chemical foaming agents generate heat during the decomposition process. They liberate more gas per gram of foaming agent than endothermic agents and produce higher gas pressure.
- Accelerators are additives increasing rate of decomposition of blowing agent or reducing its decomposition temperature. In PVC they are usually part of stabilizing system, and they are called kickers. The term accelerator is also used in curing systems for example in polyurethanes and rubbers.

- Activators are used for the same purpose as accelerators to reduce the decomposition temperature of blowing agent. Zinc oxide is the most common activator.
- The catalyst is used in polyurethane formulation to regulate the rate of production of gaseous products of reaction between isocyanates and water (blowing agent). Catalysts are also used in polyurethanes to regulate rate of cure due to the reaction between isocyanate and polyol. Both reaction rates are synchronized to produce quality foams.
- Nucleating agents are used to control foam density and provide uniform cell size. Talc is the most common example. Nucleating agents have also other function useful in the foam production as they increase crystallization rate and reduce spherulite size.

Foaming technology makes use of all three states of matter. Carbon dioxide is the best example, considering its use in the form of gas, supercritical liquid, and solid (dry ice). All these forms are used on industrial scale. Water is also a popular blowing agent because of its low cost and affinity to many materials because it can form hydrogen bonding which helps in a uniform distribution in the matrix material. The liquid form of blowing agent is very useful because it simplifies homogenization. Solid materials, especially azodicarbonamide, are also very popular in many applications.

Foaming processes can be controlled by many parameters, including type, amount of foaming agent, additives, saturation pressure, desorption time, die pressure, die temperature, feed ratio, gas contents, its flow rate and injection location, internal pressure after foaming, mold pressure, mold temperature, viscosity of composition under processing conditions, surface tension, time-temperature regime, and many other.

The selection of formulation depends on mechanisms of action of blowing agents and foaming mechanisms, as well as dispersion and solubility of foaming agents and foam stabilization requirements.

Foaming processes include the most frequently used extrusion and injection molding, but many other processing methods are also used, such as compression molding, depressurization, free foaming, microwave expansion, hot press, rotational molding, or the simple addition of pre-expanded spheres, or spheres which can be expanded during normal production conditions.

At least, forty polymers and their blends are involved in applications of foaming technologies, but the field is much broader, including such diverse materials as concrete, many food products, metal products, insulating materials, sponges, etc. The foaming processes usually decrease mechanical properties and increase compression set in materials but shape memory foams are also produced.

The above and many other topics are discussed in the fifteen chapters of the book which includes theoretical and practical information. Data on the raw materials used in their production are included in **Databook of Blowing and Auxiliary Agents**.

2

# Chemical Origin of Blowing Agents

The basic properties of blowing agents and auxiliary agents include general information, physical and chemical properties, health effects, ecological impact, and use. The detailed information on more than 350 blowing and auxiliary agents can be found in a separate book entitled **Databook of Blowing and Auxiliary Agents**.[1]

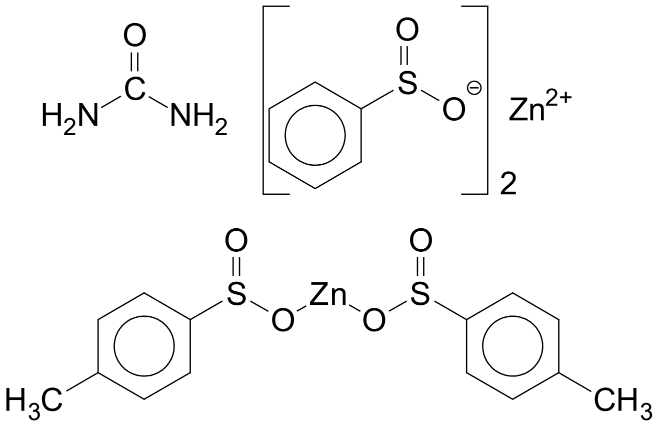
Here are tables characterizing properties of the major groups used in these applications. The data are the averages for products included in the group. It is important to consider how additives can be grouped in this section. Blowing agents are very frequently mixtures of several components, which include not only blowing agent(s) but also all auxiliary agents required to attain performance criteria selected by the product designer. Even up to 15 components are known to be mixed together to create the desired product. In some cases products contain only one component or just a few. Tables below are arranged in the alphabetical order as to assist the reader in an easier finding of the group. Blowing agents are grouped according to the chemical component which is used in the highest concentration. If the composition is not known products are qualified as "Proprietary", and this group has the most diverse and broad properties, as well as it is by far the most abundant group of all blowing agents. The auxiliary agents included in the sample are not so numerous as blowing agents and the average data included for them are reported under the general name of additive (e.g., activator, crosslinker, kicker, etc.) to show general properties of such additives.

The data in this chapter are for comparative purposes to assist in the general selection of the products but for particular purposes of application of these additives, Databook of Blowing and Auxiliary Agents should be consulted or otherwise information can be obtained by searching the open literature. The following tables are included below:

- activators
- azodicarbonamides
- crosslinkers
- dinitroso pentamethylene tetramines
- gasses
- hydrazides
- hydrocarbons
- hydrochlorofluorocarbon
- hydrofluorocarbons
- kickers

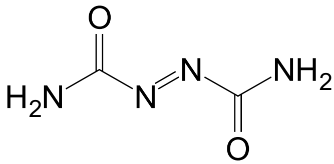
- methyl formates
- microspheres
- nucleating agents
- peroxydicarbonate
- peroxyhexanoate
- propionitrile
- proprietary
- salts of carbonic and polycarbonic acids
- sodium hydrogen bicarbonate
- sulfonylsemicarbazides
- surfactant
- tetrazoles
- water

## 2.1 ACTIVATORS



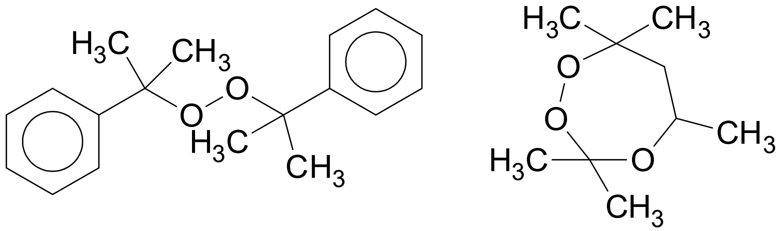
| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: carbamide (urea compound), zinc 2-ethylhexanoate, zinc benzenesulfinate, zinc carbonate, zinc ditolyl sulfinate, zinc oxide, zinc stearate | | **RTECS number**: YR6250000 |
| **Composition**: up to 98 wt% | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **Melting**, °C: 218-265 | | **Decomposition**, °C: 133-142 |
| **State**: solid or dispersion | **Color**: white to yellow | **Odor**: odorless to slight odor |
| **Density** at 25°C, kg/m$^3$: 1050-1323 | | |
| **HEALTH & SAFETY** | | |
| **Flash temp.**, °C: 127 | | **Oral**, rat LD50, mg/kg: >5000 |
| **UN risk**: R36/37/38 | **UN safety**: S26,S36/37/39 | |
| **ECOLOGICAL IMPACT** | | |
| **Atmospheric life**, years: 14 | **Partition**, log $K_{ow}$: -2.97 to -2.26 | |
| **Global warming potential**: 1320 | | **Ozone depletion potential**: 0 |
| **Algae**, LC50, mg/l: 10000/72H | | |
| **USE** | | |
| **Recommended for polymers**: EPDM, NBR, PE, PVC, PVC/NBR, rubber, SBR | | |
| **Recommended for products**: automobiles, electric and electronic products, housing products, vibration-proof material, cushioning material, sealing material, heat insulating material, noise insulation material, closure sealing gaskets for food containers, paper and paperboard | | |
| **Processing methods**: extrusion, blow molding | | |
| **Concentrations used**, phr: 1-4.5 | | |

## 2.2 AZODICARBONAMIDE



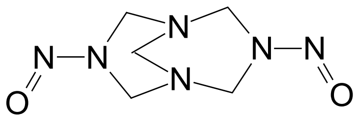
| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: azodicarbonamide | | **Character**: exothermic |
| **Composition**: 10-99.1 wt%; azodicarbonamide pasted with mineral oil; coated with dispersing agent; in PS, NBR, silicone, LDPE, EVA or EPDM carrier; in combination with other blowing agent (e.g., DNPT, OBSH, or TSH) | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **Decomposition**, $^o$C: 130-230 | | |
| **State**: paste, solid | **Color**: white to yellow to orange | |
| **Density** at 25$^o$C, kg/m$^3$: 1030-1650 | | **Max. gas yield**, $^o$C: 210 |
| **Total gas evolution**, ml/g: 44-320 (basic grades 230) | | **Max. gas evolution**, $^o$C: 199-208 |
| **Main gaseous product**: $N_2$, $NH_3$, CO, $CO_2$, $H_2O$ | | **pH**: 6.5-7.5 |
| **Refractive index** at 20$^o$C: 1.762 | | |
| **Water solubility** at 20$^o$C, g/l: 0.2 | | |
| **Vapor pressure** at 20$^o$C, kPa: 0.9456 | | |
| **HEALTH & SAFETY** | | |
| **HMIS**, F/H/R: 2/1/0 | **NFPA**, F/H/R: 1/1/0 | **Carcinogenicity**: no |
| **Oral**, rat LD50, mg/kg: >6400 | | |
| **UN risk**: R42,R44 | **UN safety**: S2,S22,S24,S37 | **UN/NA class**: 1325/3242 |
| **ECOLOGICAL IMPACT** | | |
| **Global warming potential**: 4000 | | |
| **USE** | | |
| **Recommended for polymers**: ABS, acrylics, CR, IIR, LDPE, LLDPE, MDPE, PA, PE, PP, PS, PVC-plastisols, PVC/NBR, PVDC, EVA, EPDM, NR, SBR, NBR, silicone rubber, TPE, TPV | | |
| **Recommended for products**: apparel, automotive applications, carpet, expanded sheet, flooring sealants, foam coated wire, foamed film, food trays, gaskets, leather, lunch boxes, pipe, rod, shoe midsole, tool handles, upholstery, vinyl wall covering, wire insulation | | |
| **Processing methods**: rotational molding, PE: injection molding, as well pressure, extrusion, powder & atmospheric; EPDM & EVA extrusion molding; PP pressure molding, calender molding, fluidized bed coating | | |
| **Concentrations used**, wt%: 0.5-3 and up | | |

## 2.3 CROSSLINKERS




| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: dicumyl peroxide; 3,3,5,7,7-pentamethyl-1,2,4-trioxepane | | |
| **Composition**: ~40% dicumyl peroxide; ~95% 3,3,5,7,7-pentamethyl-1,2,4-trioxepane | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **State**: solid or liquid | **Color**: white to off white | **Odor**: faint |
| **Density** at 25°C, kg/m$^3$: 950-1530 | | **Start of decomposition**, °C: 30 |
| **HEALTH & SAFETY** | | |
| **Flash temp.**, °C: 41.5 | | **UN/NA class**: 3077 |
| **ECOLOGICAL IMPACT** | | |
| **Partition**, log $K_{ow}$: 2.4 | | |
| **USE** | | |
| **Recommended for polymers**: LLDPE, HDPE, PP, natural and synthetic rubbers | | |
| **Recommended for products**: wire & cable | | |

## 2.4 DINITROSO PENTAMETHYLENE TETRAMINE COMPOUNDS

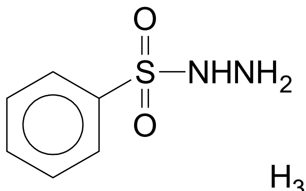


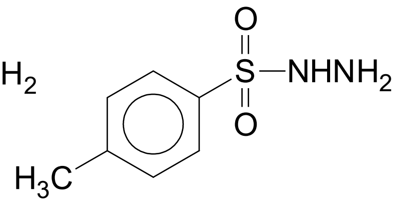
| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: N,N´-dinitrosopentamethylentetramine | | **Character**: exothermic |
| **Composition**: dinitroso pentamethylene tetramine and surface treated urea activator | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **State**: solid | **Color**: white to light yellow | **Decomposition**, °C: 120-210 |
| **Density** at 25°C, kg/m$^3$: 1450-1540 | | |
| **Max. gas yield**, °C: 210 | **Total gas evolution**, ml/g: 111-285 | |
| **Main gaseous product**: $N_2$, $NO_x$, CO, HCHO | | |
| **pH**: 7-9 | **Water solubility** at 20°C, g/l: slightly soluble | |
| **HEALTH & SAFETY** | | |
| **Oral**, rat LD50, mg/kg: >240 | | **UN/NA class**: 3224 |
| **USE** | | |
| **Recommended for polymers**: CR, EPDM, EVA, NR, SBR, NBR, PB, PE, PVC flexible | | |
| **Recommended for products**: pressurized foam, cellular rubber, soles for beach sandals, sponges | | |
| **Processing methods**: extrusion molding | | |

## 2.5 GASSES

| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: carbon dioxide (gas, liquid, solid), nitrogen | | |
| **RTECS number**: FF6400000, QW9700000 | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **State**: gas, liquid solid | **Boiling**, °C: -210.01 to -78.5 | **Odor**: odorless |
| **Color**: colorless to white (solid) | | **pH**: 3.2-3.7 |
| **Density** at 25°C, $kg/m^3$: 1.1848-1.8714 (gas); 1256.74 liquid at -20°C; 1562 (solid) | | |
| **Dissociation constant** ($pK_a$): 6.35 and 10.33 | | **Relative permittivity**: 1-1.6 |
| **Refractive index** at 20°C: 1 | **Water solubility** at 20°C, g/l: 0.02-2 | |
| **Surface tension**, mN/m: 8.85-16.2 | | |
| **Specific heat**, kJ/kg K: 0.709-1.4 | | |
| **Thermal conductivity**, W/m K: 0.0146-0.0238 | | |
| **Vapor pressure** at 20°C, kPa: 5729.1 | | |
| **Viscosity** at 0°C, mPa s: 1.37E-04; 1.66E-04 | | |
| **Critical point**, kPa/°C: 7377/30.98; 3396/-146.96 | | |
| **HEALTH & SAFETY** | | |
| **Autoignition**, °C: not applicable | | **Flash point**, °C: not applicable |
| **HMIS**, F/H/R: 0/0-3/0-1 | **NFPA**, F/H/R: 0/0-3/0-1 | **Carcinogenicity**: no |
| **OSHA**, PEL, ppm: 5000 | **Inhalation**, rat LC50, mg/kg: 90000/5M | |
| **UN/NA class**: 1013, 2187, 1845; 1066, 1977 | | |
| **ECOLOGICAL IMPACT** | | |
| **Ozone depletion potential**: 1 | | **Partition**, log $K_{ow}$: 0.83; 0.67 |

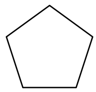
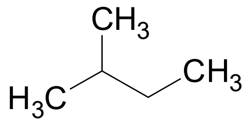
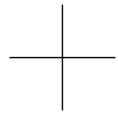
## 2.6 HYDRAZIDES




| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: p,p´-oxybisbenzenesulfonylhydrazide; p-toluenesulfonylhydrazide | | **Character**: exothermic |
| **RTECS number**: DB7321000; MW0210000 | | |
| **Composition**: hydrazide pasted with mineral oil (up to 25%); up to 98 wt% hydrazide; 30-75 wt% in carrier resin (e.g., EPDM or EPR) | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **Melting**, $^{o}$C: 60-103 | **Boiling**, $^{o}$C: 125 | **Decomposition**, $^{o}$C: >100-164 |
| **State**: solid | **Color**: colorless to white | **Odor**: geranium-like |
| **Density** at 25$^{o}$C, kg/m$^3$: 1250-1550 | | **pH**: 6-8 |
| **Total gas evolution**, ml/g: 120-150 | | |
| **Main gaseous product**: $N_2$, $CO_2$, $H_2O$ | | |
| **Water solubility** at 20$^{o}$C, g/l: insoluble | | |
| **Max. gas evolution**, $^{o}$C: 150-160 | | |
| **Critical point**, kPa/$^{o}$C: | **Vapor pressure** at 20$^{o}$C, kPa: | **Viscosity** at 20$^{o}$C, mPa: |
| **HEALTH & SAFETY** | | |
| **HMIS**, F/H/R: 3/1/1 | **NFPA**, F/H/R: 3/1/2 | **Carcinogenicity**: no |
| **Oral**, rat LD50, mg/kg: >240 | **UN/NA class**: 3224 | |
| **USE** | | |
| **Recommended for polymers**: CR, EPDM, EVA, IIR, NR, SBR, NBR, PE, PVC plastisols, silicone rubber | | |
| **Recommended for products**: sponge rubber cosmetic puffs, electrostatographic toners, buoyant seats, insulation and packing materials, adhesives, sealants, and leather substitutes, high-performance rubber sheet, NBR-PVC pipe insulation, wire insulation, neoprene-blended EPDM for automotive, press-cured NBR-PVC for flotation and athletic padding, SBR rubber rug underlay, casting for PVC carpet underlay, EVA shoe mid-sole and latex foaming, coaxial cables, cellular rubber articles in which the bright color of the final product is important | | |
| **Processing methods**: rotational molding, pressure molding, extrusion, injection molding | | |
| **Concentrations used**, wt%: 0.5-5 | | |

## 2.7 HYDROCARBONS

| | | |
|---|---|---|
| **GENERAL** | | |
| **Chemical name(s)**: cyclopentane, isopentane, neopentane | | **Composition**: 98-100% |
| **RTECS number**: GY2390000, EK4430000 | | |
| **PHYSICAL CHEMICAL PROPERTIES** | | |
| **Melting**, °C: -160 to -16.6 | **Boiling**, °C: 7.2-49 | **State**: gas, liquid |
| **Refractive index** at 20°C: 1.354-1.4065 | | **Odor**: sweet to odorless |
| **Density** at 25°C, kg/m$^3$: 630-751 | | **Color**: colorless |
| **Water solubility** at 20°C, g/l: 15.6 | | |
| **Thermal conductivity**, W/m K: 0.02 | | |
| **Vapor pressure** at 20°C, kPa: 45-77 | | |
| **HEALTH & SAFETY** | | |
| **Autoignition**, °C: 361 | **Flash temp.**, °C: -37 | **OSHA**, PEL, ppm: 600 |
| **HMIS**, F/H/R: 3/2/0 | **NFPA**, F/H/R: 3/1/0 | **Carcinogenicity**: no |
| **UN risk**: R11,R36/38 | | **UN/NA class**: 1146 |
| **ECOLOGICAL IMPACT** | | |
| **Atmospheric life**, days: 3 | **Kyoto compliant**: yes | **Montreal compliant**: yes |
| **Global warming potential**: 3-11 | | **Ozone depletion potential**: 0 |