



**WTConsulting GMBH**

WIETSCHORKE TSCHECH & PARTNER

Consultants in Regulatory Affairs and Science

## **Safety Assessment**

### **GASODOR® S-FREE**

#### **Exposure of consumers, workers, environment**

Product of

**Th. Geyer Ingredients GmbH & Co. KG**

Im Wesertal 11

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Assessment prepared by

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## Objective

Gasodor® S-Free is an odorant mixture which is added to natural gas at a maximum concentration of 7 ppm to give a warning smell to the gas. The main ingredients are ethylacrylate (CAS-Nr. 140-88-5) and methylacrylate (CAS-Nr. 96-33-3) which are contained in the product in concentrations of > 50% and 25-49%, respectively. Both substances are listed in Annex VI of the CLP Regulation No. 1272/2008 [1]. In the frame of their REACH registrations additional studies on toxicological and eco-toxicological properties were performed. The results led to more stringent classification than currently provided in the CLP Regulation for both substances.

In 2009 WTC Consulting has prepared a safety assessment in view of the skin sensitising properties and a possible respiratory sensitization potential [2]. It was concluded that respiratory sensitization is not to be expected in the case that consumers were exposed to Gasodor® S-Free if it entered ambient air via non-burned natural gas. This conclusion was confirmed in further observations.

The more stringent classification of the acrylic acid esters refers to acute inhalation exposure and environmental exposure: „toxic if inhaled, H331“ (acute toxicity category 3) and „harmful to aquatic life with long lasting effects, H412“ (chronic aquatic toxicity category 3). In the current assessment the possible impacts of the more stringent classification of Gasodor® S-Free on consumer safety as well as on safety of workers handling concentrated Gasodor® S-Free and on the environment are considered.

## Classification of Gasodor® S-Free

In the following table the classification of Gasodor® S-Free correlating to the (still) current classification of the acrylic acid esters in regulation 1272/2008 is opposed to the new classification resulting from the new classification of ethylacrylate and methylacrylate as given in the actual safety data sheets.

Classification criteria	Current classification	New classification
Flammable liquids	category 2 H225	category 2 H225
Acute toxicity, oral	category 4 H302	category 4 H302
Acute toxicity, inhalation	category 4 H332	category 3 H331
Acute toxicity, dermal	category 4 H312	category 4 H312
Skin irritation	category 2 H315	category 2 H315
Eye irritation	category 2 H319	category 2 H319
Skin sensitisation	category 1 H317	category 1 H317
Specific organ toxicity	category 3 H335	category 3 H335
Chronic aquatic toxicity	---	category 3 H412

## Assessment of consumer safety

After preparation of the safety assessment in 2009 further tests on acute inhalation toxicity of ethylacrylate and methylacrylate were performed. The results led to new classification of both acrylate esters from category 4 (H332 harmful if inhaled) to category 3 (H331 toxic if inhaled), leading to labelling of both substances with the hazard pictogram GHS06 for acute toxicity. This classification in category 3 is based on an acute lethal effect to half of the animals ( $LC_{50}$ ) exposed to concentrations between 2 mg/l and 10 mg/l (or between 500 ppm and 2'500 ppm) during a period of 4 hours [1].

In the safety assessment of 2009 the maximum acute exposure of consumers, end users of odourised natural gas, to Gasodor® S-Free was calculated. For a short time, i.e. for few minutes, the concentration could amount to 0.0035 ppm. Thus the lethal concentration ( $LC_{50}$ ) as determined in the animal tests after 4 hours exposure was at least 140'000 times higher. An acute hazard for consumers by short term inhalation of a low concentration of Gasodor® S-Free in ambient air is unlikely.

In the safety assessment of 2009 it was concluded that short term exposure of consumers to Gasodor® S-Free is not expected to result in respiratory sensitisation. In addition a safety margin of at least 1'400 was calculated between consumer exposure and the maximum workplace concentration\*. Last year a new evaluation of ethylacrylate was performed by the MAK-Commission [3]. On the one hand in this evaluation it is pointed to the fact that since 1999 still no cases of respiratory sensitisation were reported. On the other hand the maximum workplace concentration was reduced from 5 ppm to 2 ppm based on new data obtained on irritation of nose and eyes with human volunteers. After reduction of the maximum workplace concentration there still remains a safety margin of 570 between the maximum expected consumer exposure and the maximum workplace concentration.

The new data on acute lethal toxicity of ethylacrylate and methylacrylate as well as the reduced maximum workplace concentration of ethylacrylate do not imply a reduction of consumer safety. The safety margin to concentrations posing a health concern remains sufficiently large.

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\* The maximum workplace concentration corresponds to the maximum concentration of a chemical substance in the workplace air which generally does not have known adverse effects on the health of the employee even when the person is repeatedly exposed during long periods, usually for 8 hours daily but assuming a 40 hour working week [4]. The new maximum workplace concentration was published in the latest version of the list of MAK values 2015 but was not yet included in TRGS 900 (Technische Regeln für Gefahrstoffe).

## **Safety at the workplace when handling the concentrated product Gasodor® S-Free**

The main hazards of concentrated Gasodor® S-Free come from the flammability of the liquid mixture as well as from the high vapour pressure which can lead to explosive mixtures in air. In addition to dermal exposure workers also may be exposed by inhalation of vapours. Gasodor® S-Free is irritant to eyes, nose and skin.

For the safe handling of such products detailed instructions do exist for the respective workplaces. Gasodor® S-Free consists of the main constituents ethylacrylate and methylacrylate and the classification and labelling of the mixture is identical with those of the constituents. For Gasodor® S-Free the same precautions for safe handling do apply as for the individual acrylates. The safety instructions are detailed in the safety data sheets.

From the new and more stringent classification of ethylacrylate and methylacrylate and accordingly of Gasodor® S-Free in category 3 instead of category 4 for acute inhalation toxicity no changes do result regarding the precautions for safe handling at the workplace compared to those already existing. When handling Gasodor® S-Free the workplace always has to be well ventilated. If this cannot be achieved sufficiently personal respiratory equipment has to be used. In addition always safety glasses have to be worn, where required face shield. For skin protection chemical resistant gloves have to be worn, where necessary chemical resistant apron, boots, protective clothing. Remove and wash contaminated clothing before re-use. Wash hands immediately after handling the product and before breaks.

Due to their irritating effects on eyes and nose the maximum workplace concentrations for both acrylates are limited to 5 ppm each. Last year the limit for ethylacrylate was set at 2 ppm by the MAK-commission based on new study results on irritation of eyes and nose obtained with human volunteers [4]. The new classification of both acrylates in category 3 for acute inhalation toxicity was based on animal tests in which the acute lethal concentration after a 4 hour exposure period to ethylacrylate or methylacrylate was determined to range between 500 ppm and 2'500 ppm. Thus the lethal concentrations as determined in the animal tests were at least 100 times higher than the maximum workplace concentration of 5 ppm. Since irritation of eyes and nose starts already at a concentration of approx. 5 ppm it can be expected that workers will not stay for longer periods in areas where higher concentrations are prevailing that were lethal in the animal tests.

When the safety precautions according to the safety data sheet for avoidance of dermal and inhalation exposure during handling of Gasodor® S-Free will be followed no impairment of worker health is to be expected. The classification of Gasodor® S-Free in category 3 for acute inhalation toxicity does not require additional safety measures for handling of the concentrated product Gasodor® S-Free.

Further information on ethylacrylate and methylacrylate and its safe handling is described in a brochure of the European Basic Acrylic Monomer Group (EBAM) [5].

## Safe handling of the concentrated product Gasodor® S-Free at the workplace in view of environmental exposure

According to the new classification of Gasodor® S-Free for chronic aquatic toxicity category 3 („harmful to aquatic life with long lasting effects, H412“) the mixture has to be labelled with the precautionary statements P273 (avoid release to the environment) and P501 (dispose of contents/container to .....). No changes in the handling are required.

When the safety measures as described in the respective exposure scenarios of the extended safety data sheets will be followed during handling of Gasodor® S-Free it can be assumed that the limits of tolerable concentrations in aquatic systems (PNEC, Predicted No Effect Concentration) will be met and that there will be no environmental hazard.

### Instructions for transport and storage

From the new and more stringent classification of ethylacrylate and methylacrylate and accordingly of Gasodor® S-Free in category 3 instead of category 4 for acute inhalation toxicity as well as category 3 for chronic aquatic toxicity no changes do result regarding the precautions for transport and safe storage compared to those already existing. The old and new provisions for transport labelling of the hazardous product Gasodor® S-Free are the following:

Transport hazard class	ADR 3	RID 3	IMDG 3	IATA-DGR 3
Packaging group	ADR II	RID II	IMDG II	IATA DGR II
UN Number	1266			

Further information on ethylacrylate and methylacrylate is described in the EBAM brochure [5]. It can be assumed that the information provided for the individual substances also covers the mixture since the physical-chemical properties of both substances are very similar.

### Further provisions

Based on the new classification of the acrylates and of Gasodor® S-Free in category 3 for acute inhalation toxicity Gasodor® S-Free falls under Directive 2012/18/EU [6]. The qualifying quantity for lower-tier requirements starts at 50 t, that for higher-tier requirements at 200 t.

### Summary

The main hazards of concentrated Gasodor® S-Free come from the flammability of the liquid mixture as well as from the high vapour pressure that can lead to explosive mixtures in air. In addition to dermal exposure workers also may be exposed by inhalation of vapours. Gasodor® S-Free is irritant to skin and mucous membranes. Irritation of eyes and nose was

observed in humans already at a concentration of 5 ppm ethylacrylate. Based on new studies both acrylates were recently classified in category 3 for inhalation toxicity (H331) and in category 3 for chronic aquatic toxicity (H412).

For handling of Gasodor® S-Free at the workplace, during transport and storage already stringent safety precautions do exist based on its flammability and its irritating effects to skin and mucous membranes. In addition Gasodor® S-Free has a very low odour threshold value, and the smell is very unpleasant. Due to the already existing stringent safety precautions and on the early perception of smell and irritation of eyes and nose the new classifications H331 and H412 do not imply changes in the handling of Gasodor® S-Free. Direct contact of skin and eyes has to be avoided. The workplace concentration for acrylates has to be met. The product may not be released to the environment.

When the safety precautions at the workplace will be adhered to no adverse effects on the health of workers who handle concentrated Gasodor® S-Free are to be expected neither from acute exposure nor from repeated and long term exposure. Additionally, the new classification of Gasodor® S-Free does not have any influence on the safety of consumers of natural gas odourised with Gasodor® S-Free.

A handwritten signature in blue ink, appearing to read 'A. Tschech', with a stylized flourish at the end.

Dr. Andreas Tschech

## References

- [1] REGULATION (EC) Nr. 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures
- [2] Safety assessment GASODOR® S-FREE (2009), WTConsulting GmbH, Switzerland
- [3] Ethylacrylat, Nachtrag 2016 in: The MAK Collection for Occupational Health and Safety 2016, Vol 1, No1; doi 10.1002/3527600418.mb14088d0060
- [4] List of MAK and BAT values 2015, Deutsche Forschungsgemeinschaft, Report no. 51
- [5] Brochure: Safe Handling and Storage of Acrylic Acid Esters, 3<sup>rd</sup> Ed. (2015), European Basic Acrylic Monomer Group  
[http://www.petrochemistry.eu/about-petrochemistry/products.html?filter\\_id=7](http://www.petrochemistry.eu/about-petrochemistry/products.html?filter_id=7)
- [6] DIRECTIVE 2012/18/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on the control of major-accident hazards involving dangerous substances