

Since the eighties ATOFINA manufactures sodium methylmercaptide (SMM).

SMM is used as thiomethylation agent in a variety of applications. It represents the alternative for methylmercaptan, in cases where transport or storage of methylmercaptan are restricted.

In thiomethylation reactions by organic substitution the methylthiolate ion is one of the reactants. In such cases SMM can be used directly. In organic addition reactions the SMM should be to acidified in order to obtain the free methylmercaptan prior to the thiomethylation reaction.

Elf Atochem offers four grades of SMM : aqueous solutions of 21, 33 or 54%, and a 21% methanolic solution. SMM 21% and SMM 33% are commercially available, SMM 21% methanolic are produced on a pilot unit and SMM 54% are on advanced development.

Your choice of the preference will depend on the situation at your production site. This brochure combines the many years of experience of ATOFINA Production, Logistic, Application and Research employees, and aims to help you making that choice.

SMM (Sodium methylmercaptide)

Physical and chemical properties

SMM commercial grades

Formula: CH_3SNa
CAS No: 5188-07-8
EINECS: 225-969-9
TSCA 5188-07-8

Item	SMM-21 (aqueous)	SMM-33 (aqueous)	SMM-54 (aqueous)	SMM-21 (methanolic)
SMM [wt%]	20.7 - 21.3	32.3 - 34.0	52.0 - 54.0	min. 21.0
NaOH [wt%]	max. 1.0	max. 1.5	max. 3.0	max. 0.8
Water [wt%]				max. 10%

Packaging

SMM-21 (aqueous)	SMM-33 (aqueous)	SMM-54 (aqueous)	SMM-21 (methanolic)
Heated isocontainers 200 L metal drum with PE inner drum, 210 kg net	Heated isocontainers	Heated isocontainers	200 L metal drum with PE inner drum, 180 kg net

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Physical properties

property	SMM-21 (aqueous)	SMM-33 (aqueous)	SMM-54 (aqueous)	SMM-21 (methanolic)
Crystallisation temperature	0 °C	35 – 40 °C	Approx. 55 °C	
Relative density	1.10 (20°C)	1.203 (20°C, solid) 1.181 (50°C) 1.171 (60°C)	1.25 (70°C) 1.324 (20°C)	0.946 (20°C)
Viscosity	6.02 cP (20°C)	4.0 cSt (50°C) 3.45 cSt (55°C) 3.0 cSt (60°C)	12.850 cSt (65°C) 10.200 cSt (70°C) 8.314 cSt (75°C)	6.32 cP (20°C)
Decomposition temperature		210°C	> 210°C	200°C
Decomposition enthalpy		-200 J/g	< -256 J/g	-450 J/g
Dissolution enthalpy		-170 J/g	-165 J/g	
Auto-ignition temperature			> 350°C	422°C
Flash point (ASTM D 93)	27°C	50°C	> 23°C	14°C
pH	11	—14	—14	12.4
Boiling point		85°C	69°C	64.7°C

Stability

SMM is a stable product. DSC tests show decomposition only at temperatures above 200°C. SMM does not contain stabilisers.

However SMM readily oxidises when in contact with air, yielding Dimethyldisulfide (CH_3SSCH_3), which results in turbidity or, even under not too extreme circumstances, in an oil layer on top of the aqueous SMM phase. For this reason, SMM in containers is blanketed under nitrogen.

Also sampling and manipulation for QC purposes may easily lead to air oxidation, and as a consequence, erroneous analytical results.

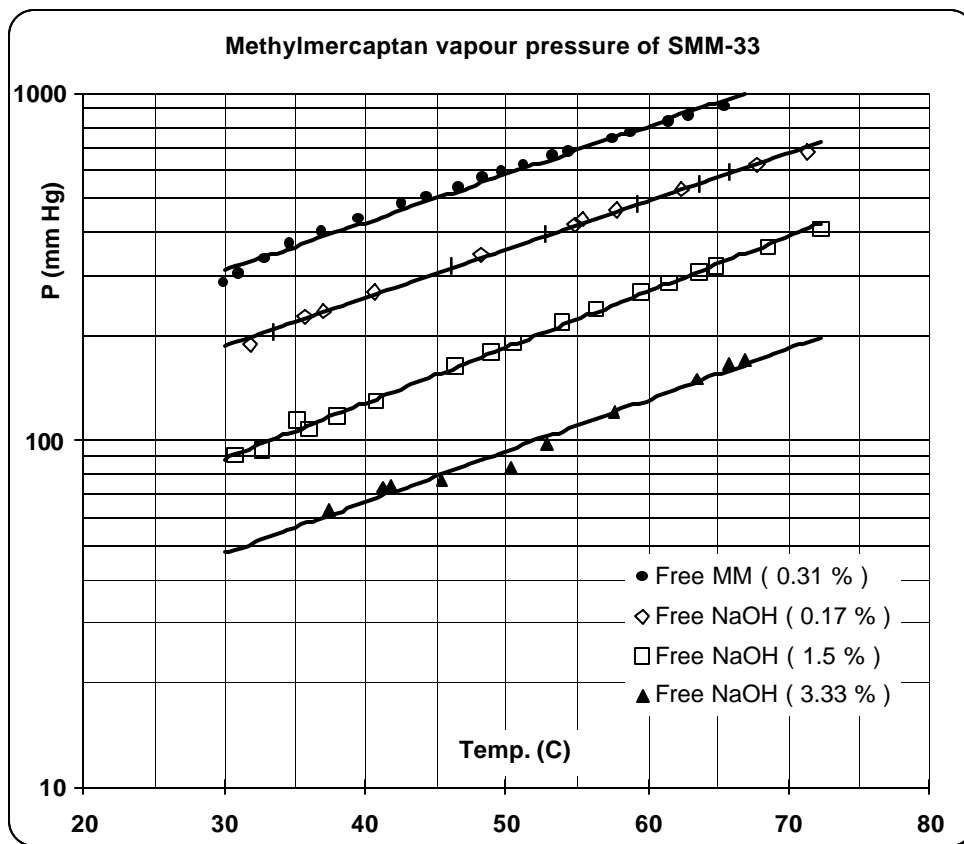
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Vapour pressure

Methylmercaptan vapour is present above SMM, as a result of ionic and gas -vapour equilibria;



In order to reduce MM vapour pressure, a slight excess of NaOH is always present in SMM.

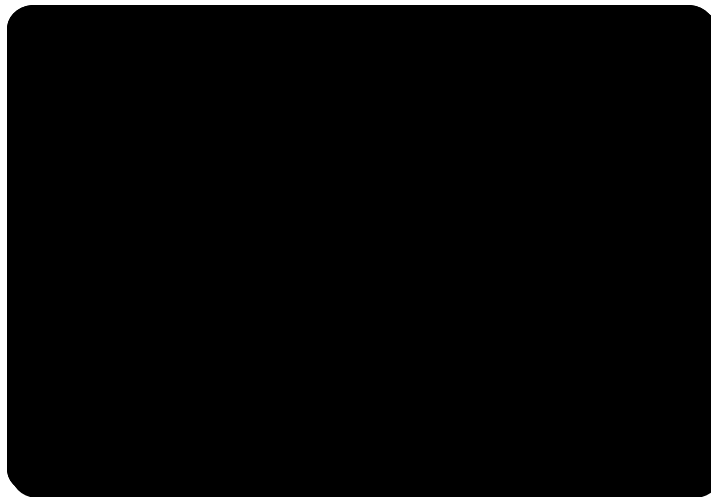


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Solubility in water

The SMM crystallisation temperature varies a few degrees according to the free NaOH concentration. SMM crystallises as a hydrate $\text{CH}_3\text{SNa} \cdot 4.5 \text{H}_2\text{O}$, i.e. as 46%. Upon solidification due to cooling during transport and storage, SMM-33 is initially present as an homogeneous mixture of amorphous solid and mother liquid. Crystallisation is very slow. Only after a period of several months, phase separation takes place (separation of mother liquid top layer) as the result of crystallisation. In this case reheating without agitation of the container content will lead to an inhomogeneous product.



Corrosion tests

A gravimetric test and stress corrosion cracking test of SMM-33 with a U-curved SS-316 Ti test piece, according ASTM G30, for 21 days at 75°C do not show any significant corrosion. Gravimetric test SMM-50% on SS-316 L, 7 days at 70 and 120°C showed no significant corrosion. SMM-50% on Carbon steel (7 days at 70°C) showed severe pitting and weight decrease; also discoloration of product.

Materials for connections :

Piping: SS316

Hoses SS316

Pump: Heated SS316 centrifugal pump with a double mechanical seal (glycol/water as seal liquid). It is recommended to heat the seal system as well.

Gaskets: Spiral wound

Dry break couplings: SS316 with Kalrez gaskets.
Chemical resistance of Viton is moderate to poor.

Container reheating and discharge

Handling of aqueous SMM in containers is based on:

1. Product classification (corrosive, flammable liquid or solid).
2. Vapour pressure and odour of the product.
3. Crystallisation temperatures for the various grades.
4. Air oxidation of SMM.

Reheating may be done with steam of 1 bar or preferably with hot water.

Discharge either by pump or by nitrogen pressure. Avoid contact with air.

Depending the local conditions and regulations, connect the vapour exhaust line to a flare, a bleach scrubber or active carbon filter.

For detailed information please contact your local ATOFINA agent.

Version 0

Les valeurs mentionnées dans ce document sont le résultat d'essais conformes aux usages en matière d'études : elles sont données à titre indicatif afin de permettre à notre clientèle le meilleur emploi de nos produits et doivent être considérées comme des valeurs moyennes fournies sans engagement de notre part.

The values given in this document have been obtained in laboratory tests conforming to standard procedures ; they should be regarded as mean values given as an indication to customers of the best ways of using our products. They do not imply any undertaking on our part.

This document do not replace the safety data sheets.

