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**DHTDMAC:- Aquatic and
Terrestrial Hazard Assessment
CAS No. 61789-80-8**

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DHTDMAC

AQUATIC AND TERRESTRIAL HAZARD ASSESSMENT

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DHTDMAC: AQUATIC AND TERRESTRIAL HAZARD ASSESSMENT

SECTION 1. SUMMARY AND CONCLUSIONS

Dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC) is almost exclusively used as a fabric softener in the household laundry rinsing process. Consequently the chemical is widely dispersed and may reach the aquatic and terrestrial environment following sewage treatment. This report refers to data related to the time period when the highest quantities (approx. 50,000T/year) of DHTDMAC were consumed in Europe. Since 1990 changes in the fabric softener formulations on the European market have resulted in a 80-90% decrease of consumption.

Due to its physical and chemical properties DHTDMAC adsorbs strongly onto surfaces and easily forms complexes with anionics such as alkylsulfonates or natural humic acids.

In standard laboratory tests, DHTDMAC is not readily biodegradable but in the presence of adapted biomass it shows total mineralization in up to 200 days.

In sewage treatment an average of 95% of DHTDMAC is removed from waste water. A large part of this removal is due to adsorption on sludge solids. Mass balance studies suggest that primary biodegradation in the biological step of sewage treatment may be significant.

In river water systems 70% of primary biodegradation was observed after 40 days. This result is consistent with mineralization studies performed without and with sediments showing respectively 10 and up to 65% conversion of ^{14}C α -alkylcarbon into $^{14}\text{CO}_2$.

Studies performed in soil indicated that 50-60% mineralization occurs in 120-430 days.

The highest environmental concentrations were found in waste water. The mean concentrations are normally around 1mg/l; exceptionally they may reach 4mg/l. Concentrations in effluents are generally in the order of 0.05mg/l.

The concentrations measured in rivers in different countries vary between 0.002 and 0.04mg/l depending on the sites, river size etc. In some low velocity systems e.g. canals and polders substantially polluted by other chemicals, concentrations of DHTDMAC up to 0.1mg/l have been measured.

The laboratory results on aquatic toxicity of DHTDMAC are highly dependent on the test conditions, sample preparation and presence of impurities.

The chemical appears to be very toxic especially to algae when tested only in laboratory water, whereas in natural waters, effects may be observed only at concentration 2-3 orders of magnitude higher. The lowest NOEC in laboratory water was observed with *Selenastrum capricornutum* (0,006mg/l). In treated sewage effluent diluted in river water it was 20.3mg/l. In the same effluent diluted river water the NOEC for the most sensitive species *Ceriodaphnia dubia* was 4.53mg/l.

Hazard assessment of chemicals of this type present particular difficulties because of their physico-chemical properties (insolubility/adsorption/complexation) which determine their bioavailability and thus the toxic effects. Hence methods have to be adopted which take proper account of the factors applying in practical situations. For DHTDMAC such approaches lead to PNEC/PEC ratios in the range of 8-450 using conservative approaches.

Terrestrial organisms, higher plants and earthworms exposed to DHTDMAC in sludge amended soil, even at levels grossly in excess of those expected during normal practice, do not exhibit adverse effects in toxicity tests. There was no evidence of bioaccumulation in toxicity tests to earthworms or of impairment of the general metabolism of soil as a result of contamination with DHTDMAC.

Based on the above considerations, it can be concluded that the environmental concentration of DHTDMAC discussed do not pose a hazard to aquatic and terrestrial systems.

SECTION 2. CHEMISTRY, PHYSICO-CHEMICAL PROPERTIES AND USES

2.1. INTRODUCTION

Dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC), also called Dihardened tallow dimethyl ammonium chloride, is a commercial dialkyl dimethyl ammonium chloride in which the alkyl groups are derived from hardened tallow fatty acids. The product contains a mixture of dialkyl dimethyl quaternary ammonium compounds, with carbon chain lengths varying from C₁₄ to C₁₈, the C₁₆ and C₁₈ being the most abundant. The alkyl chains are saturated, that is, they contain no chemical double bonds.

CAS No. 61789-80-8

CAS Name: Quaternary ammonium compounds, bis (hydrogenated tallow alkyl) dimethyl chlorides.

EINECS No. 2630902

Other acronyms often wrongly used for DHTDMAC are:

- DTDMAC (Ditallow dimethyl ammonium chloride); a mixture of quaternary ammonium compounds with the same chain length distribution as DHTDMAC but with some unsaturated bonds in the alkyl chains.
- DSDMAC (Distearyl dimethyl ammonium chloride) and DODMAC (Dioctadecyl dimethyl ammonium chloride); two names for a quaternary dialkyl dimethyl ammonium compound in which the alkyl chains are saturated C₁₈ only. This substance is the major component of DHTDMAC.

These compounds are commercially available and have slightly different properties from each other and from DHTDMAC.

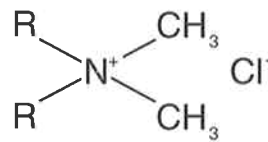
DHTDMAC contains two hydrophobic alkyl chains and a hydrophilic, positively charged, quaternary nitrogen; it has strong surface active properties. It has a low true aqueous solubility but is easily dispersed in water where it forms lamellar structures. These structures can be dispersed as single bilayer spherical vesicles or multilamellar liposomes. DHTDMAC adsorbs strongly to surfaces making them more hydrophobic. This is the basis for the technical applications of DHTDMAC of which rinse-added fabric softener has been traditionally the largest used sector.

2.1.1. Production Process

The product is manufactured from tallow fatty acids, which are reacted with ammonia and dehydrated to form an intermediate fatty acid nitrile. This is catalytically reduced with hydrogen to form a secondary amine, splitting off ammonia and saturating the double bonds in the alkyl chains. The secondary amine is methylated with formaldehyde under reductive conditions and then quarternized with methylchloride.

2.1.2. Chemical Structure and Composition

The structural formula is:



in which:

R = alkyl

The alkyl chain length distribution is:

C ₁₂	max 2%
C ₁₄	1-5%
C ₁₆	25-35%
C ₁₈	60-70%
C ₂₀	max 2%

The average molecular weight ranges from 567 to 573.

The impurities in standard European products are:

- dihydrogenated tallow methylamine and trihydrogenated-tallow amine together with the corresponding hydrochlorides, less than 2%;
- monohydrogenated tallow trimethyl ammonium chloride, less than 4% of total solids;
- trihydrogenated tallow methyl ammonium chloride, less than 4% of total solids.

2.1.3. Commercial DHTDMAC

Commercial quality DHTDMAC sold in Europe normally consists of 75-78% active substance and 10-15% isopropanol, the balance being water. It contains 0.1-0.3% sodium chloride. Its melting point is typically between 30 and 45°C.

2.2. PHYSICO-CHEMICAL PROPERTIES

Table 1 Physical Properties

	DHTDMAC, commercial grade	DHTDMAC, 100% active	DODMAC, DSDMAC, 100% active
CAS number	61789-80-8	61789-80-8	107-64-2
Mol. weight	565-570	565-573	586.48
Empirical formula			C ₃₈ H ₈₀ HCl
Active content, %	75-78	100	100
Iodine Colour No. (50 C°)	max 4		
Density, g/cm ³	0.86 (50)		0.84 (88)
Melting point, °C	30-45	50-60	72-122
Thermal stability, decomposes at, °C	~135	~135	135
pH value (10 g/l)	4-6		
Solubility at 25 °C, - water - isopropanol - ethanol - acetone - chloroform	<1µg/l ≥5% ≥5% slightly ≥5%	<1µg/l	<1 pg/l
Adsorption, K _d l/kg	85,000		12,489 3,833 10,775

2.2.1. Solubility

Because commercial DHTDMAC is a mixture of chain length homologues with extremely low aqueous solubility, the determination of its true solubility is very difficult. This explains apparently contradictory results published in the scientific literature. Kunieda and Shinoda (1978) suggested that the aqueous solubility of pure DODMAC is about 3mg/l. Later, Evans and Needham (1987) estimated the solubility of a polar lipid of similar chain length

to be less than 5.7×10^{-10} mg/l from observations made on a single vesicle in a mixture of known composition. Based on thermodynamical considerations, Laughlin *et al* (1990) concluded that the solubility of DODMAC is expected to be similar to that of this polar lipid (Laughlin *et al*, 1990). The true water solubility of DODMAC is therefore extremely low.

Aqueous solubility is affected by purity. Additionally, the shorter chain length homologues in commercial DHTDMAC are more soluble than DODMAC. Since DHTDMAC contains about 0.95 molar fraction units of two C_{16} -alkyl chains and higher homologues, this is not expected to have a significant effect on the solubility of commercial DHTDMAC. Therefore, for practical purposes, the "true" solubility of DHTDMAC can be safely considered not to exceed 10^{-3} mg/l.

2.2.2. Colloidal Properties

The colloidal properties of various dialkyl dimethyl ammonium compounds have been studied by Fontell *et al* (1986), Dubois and Zemb (1991) and Laughlin *et al* (1991). They showed that long chain dialkyl dimethyl ammonium salts exist in lamellar structures either crystalline or as liquid crystals, depending on temperature. These compounds form dispersions in water containing either unilamellar or multilamellar particles such as vesicles. The size of the dispersed particles depends on the temperature, the shear forces applied (i.e. the amount of energy put into the system) when making the dispersion and the presence of dispersants. High levels of energy (e.g. ultrasonification) produce small particle sizes.

The Krafft temperature is the temperature below which colloidal particles crystalline molecular aggregates and above which they are liquid crystals (Lindmann and Wennerstroem, 1980). The Krafft temperature of DODMAC has been determined by Laughlin *et al* (1990) to be 47.5°C. Dubois and Zemb (1991) also determined the Krafft temperature of Dialkyl dimethyl ammonium chlorides by measuring the melting point of the carbon chains in a dispersion using differential scanning calorimetry. They found 22°C for Didoceyl dimethyl ammonium chloride (DDdDMAC) and 37°C for Dihexadecyl dimethyl ammonium chloride (DHDMAC). Determination of the melting point of the carbon chains in a dispersion of DHTDMAC gave about 33-35°C (Berol Nobel, 1990).

Colloidal surfactant particles are crystalline at temperatures below the Krafft temperature. Therefore, the molecular movements in a system below its Krafft temperature are slow and the time needed to reach any physical-chemical equilibrium can be of the order of months. The actual time needed depends on factors like the size of the colloidal particles, the concentration of solid particles and the agitation in the system. Since the Krafft point

of DHTDMAC lies above room temperature, physical-chemical equilibria with DHTDMAC will be slow to reach. This explains why several authors regard the adsorption of DHTDMAC to particles to be essentially irreversible (see section 2.2.3) (Neufarth *et al*, 1978).

DHTDMAC can also form mixed aggregates with other surfactants. This is shown by the phase diagram of Sodium dodecyl sulphonate (SDS)/Didodecyl dimethyl ammonium bromide (DDdDMAB)/H₂O which shows the existence of an isotropic solution containing about 4% of DDdDMAB. DHTDMAC also can form mixed aggregates with monoalkyl trimethyl ammonium compounds (Lindman, 1992).

2.2.3. Adsorption and Desorption

Cationic surfactants, and especially the dialkyl dimethyl ammonium compounds, adsorb strongly onto surfaces. This has been studied by several authors using model systems. The adsorption of DHTDMAC in natural systems is more complex than in the models and depends on many factors such as:

- size of DHTDMAC aggregates,
- existence of mixed aggregates where DHTDMAC is associated with other surfactants,
- competitive adsorption with other surfactants,
- type of suspended particles present,
- concentration of particles,
- amount of surfactants in relation to particles,
- temperature.

Larson and Vashon (1983) studied structure/activity relationships for adsorption and biodegradation of a series of long chain quaternary ammonium compounds using radiolabelled DODMAC, hexadecyl trimethyl ammonium bromide (HTMAB) and octadecyl trimethyl ammonium chloride (OTMAC) and various sediments collected from the Ohio River and Rapid Creek together with a standard EPA sediment (EPA 18), using the method described by Games *et al* (1982).

The characteristics of the sediments which may influence adsorption were as follows:

Sediment	% Organic carbon	% Sand	% Clay	% Silt	CEC meq/100g	pH
EPA 18	0.7	34.6	39.5	25.8	15.4	7.8
Ohio River	2.0	28.0	39.7	32.4	18.4	7.1
Rapid Creek	3.5	0.2	2.4	97.4	15.7	

The adsorption results showed that the substances were extensively bound to all of the sediments:

SEDIMENT	COMPOUND	K_d (l/kg)
EPA 18	DODMAC	12,489
Ohio River	DODMAC	3,833
Rapid Creek	DODMAC	10,775

$$\text{sediment water partitioning coefficient } K_d = C_{\text{solids(mg/kg)}} / C_{\text{solution(mg/l)}}$$

Desorption experiments indicated that all compounds tested bind strongly to both organic and inorganic particulate matter (Larson and Vashon, 1983).

In another experiment DODMAC did not desorb from a 1g/l concentration dispersion of laponite (a synthetic sodium hectorite) in the presence of up to 5g/l sodium dodecyl sulphate (Capovilla *et al*, 1991).

Van Leeuwen *et al* (1990) calculated the K_d for DHTDMAC on suspended solids from data generated on samples from German rivers published by Klotz (1987a) on DHTDMAC and found it to be 8.5×10^4 l/kg.

Neufahrt *et al* (1978) studied the adsorption of radiolabelled distearyldimethyl ammonium bromide (DSDMAB) on activated sludge. More than 50% was adsorbed within 20 minutes. Equilibrium was not even reached after 280 minutes when more than 90% had been adsorbed. The initial rate of DHTDMAC adsorption to particles is high but equilibrium is reached slowly. Additionally, the desorption process is extremely slow. Their observations are in agreement with the observations described in section 2.2.2 that the Krafft temperature of DHTDMAC is higher than room temperature, causing physical-chemical equilibria to be reached very slowly.

Therefore, for practical purposes adsorbed DHTDMAC can be considered as permanently bound to particles. This creates difficulties for the analysis of DHTDMAC in environmental samples. It requires for example very powerful extraction techniques to detect the adsorbed DHTDMAC.

2.2.4. Complexing with Anionics

DHTDMAC forms complexes with anionic compounds such as anionic surfactants e.g. linear alkyl benzene sulphonate (LAS) etc, and humic acids. The complexes are neutral and have a low solubility in water. Capovilla *et al* (1991) studied the complexing of DODMAC with sodium dodecyl sulphate. They found that the addition of sodium dodecyl sulphate to DODMAC mixed in water led to the formation of insoluble complexes. Unlike complexes with monoalkyl ammonium compounds, these complexes did not dissolve in the form of mixed micelles.

Buecking *et al* (1978) showed that DHTDMAC does not adsorb onto siliceous materials in the presence of a large excess of anionic or nonionic surfactant.

2.3. USES

About 90% of the total production of DHTDMAC is used as the active component in liquid formulations of fabric softeners designed to be added to the last rinse of a machine wash cycle. Due to market changes the quantity of DHTDMAC used in Europe as fabric softener has decreased by 80%-90% in the last 3 years. Rinse-added fabric softeners come in dilute and concentrated forms containing various levels of DHTDMAC. They are manufactured by dispersing DHTDMAC in hot water together with a dispersant and adding colour and perfume. Active content in normal fabric softeners is in the range of 4-6% and in concentrates 10-22%. Nonionic surfactants (ethoxylated alcohols) can be used as dispersing agents.

On dilution in the rinse water, more than 95% of the DHTDMAC adsorbs uniformly onto cloth. This is what gives the feeling of softness and may also improve the drying of the clothes and decrease wear. The adsorbed DHTDMAC remains on cloth until the next wash when the detergent used in the wash strips DHTDMAC from the cloth. Thus the DHTDMAC used will eventually end up in waste water, always associated with detergent surfactants by forming ion pairs with anionics surfactants during the wash (see section 2.2.4).

DHTDMAC is also used as conditioning agent in personal care products such as shampoos and hair conditioners and as emulsifier in lotions. The largest industrial application is in the production of organo-clays. These are used in the oil-industry as drilling muds and by the paint industry as rheological additives. Another industrial application is in sugar refining.