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Environmental and Safety Aspects of Cationic Bitumen Emulsions			
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ABSTRACT

**ZUSAMMENFASSUNG
RÉSUMÉ**

The paper reports various studies of the safety and environmental effects associated with the use of cationic asphalt emulsions, for example in slurry surfacing.

Volatile components derived from the bitumen emulsifiers in the area around a microsuffacing job and also around a spray application of cationic rapid-setting emulsion were collected by air sampler with a specially absorbant filter. Emulsifier itself was not detected in any of the air samples. The major component detected from the microsuffacing air samples was ammonia (20ppb), together with minor amounts of alkylamines (0.2ppb). No amine components at all were detected from the spray application with emulsion.

In a separate study the amount of emulsifier in the break water from a slurry seal was measured. The level was less than 0.5ppm. No emulsifier was detected in laboratory samples designed to simulate the leaching effect of rainwater on slurry surfacings.

In another study the adsorption of cationic emulsifiers on standard soils was measured. Virtually all the cationic emulsifier was irreversibly adsorbed onto soils. This implies that even if cationic emulsifiers could "escape" from the seal they are immobilized on the soils around the road surface.

Aquatic toxicity studies of cationic surfactants similar to those used asphalt emulsions show their toxicity to be greatly reduced by adsorption onto minerals and soils.

Environmental and Safety Aspects of Cationic Bitumen Emulsions

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1. Introduction

Put in comparison with the safety and environmental impact of road transportation systems as a whole, the contributions from construction and maintenance processes are small. (1) Traffic is responsible for the greatest part of deaths and environmental damage associated with road transport and there is evidence that well-maintained roads with smooth riding surfaces lead to a reduction in accidents and an improvement in fuel consumption

But the relative environmental and safety impact of construction and maintenance techniques should not be ignored. Taken overall, bitumen emulsions are viewed favorably in terms of both safety to workers, emissions and in energy consumption/ global warming potential. For example cold manufactured bituminous road materials, whether prepared with foamed bitumen or emulsion have advantages over hot mix. Energy consumption and hence global warming potential and resource depletion are lower: a cold constructed roadway has been calculated to use only 60-70% of the energy of a hot mix roadway of similar bearing capacity (2,3). In the paving of solvent-free emulsion cold mixes, exposure of workers to hydrocarbon fumes is eliminated, although in recycling with emulsions containing diesel oil, exposure was comparable to that from hot mix (4). Field measurement has confirmed that lower paving temperatures of cold or warm mix lead to lower fume exposures (5). Early calculations suggest that microsurfacing is a more “eco-efficient” maintenance treatment than thin hot mix overlays, when structural improvements are not required. (6) The main part of the benefit comes from the lower quantity of materials applied to the road.

The picture is not completely clear-cut however, chipseal (surface dressing) with emulsion leads to less emissions of potentially ozone promoting hydrocarbons than hot bitumen or cut back bitumen treatments. And emulsions have lower fire and burn hazards. But a study by AARB suggests that for job sites very remote from an emulsion plant, the extra fuel needed to transport the water in an emulsion may lead to a higher global warming potential (7).

While there seems to overall benefits from the use of emulsions, the potential emissions from cold emulsion processes could conceivably include volatile chemicals from the emulsion entering the atmosphere and/or chemicals contained in the run-off water generated from the breaking process. Manufacture of the emulsifying chemicals and emulsions may also have an environmental impact.

This paper reports the results of several studies related to safety aspects of cationic emulsions and emulsifiers and their effect on the environment. Some of the data was reported earlier (8, 9)

2. Manufacture of Cationic Emulsifiers

Cationic emulsifiers are nitrogen-based cationic surfactants mostly derived from renewable resources such as natural fats and oils like tallow, rapeseed oils, and tall oils. Manufacture of the surfactants involves reaction of fatty acids with either ammonia or with polyethylene polyamines, which may themselves be derived from ammonia. The natural resources consumed and emissions resulting from the manufacture of a typical cationic surfactant has been calculated

(Table 1). The figures include all the data also for power generation in Sweden and in the transport of raw materials to the plant. The total energy consumed in the manufacture is around 60MJ/kg. Bitumen emulsions contain from 0.1-1.0% emulsifier as well as hydrochloric or phosphoric acids and other additives. It has been estimated that manufacture of bitumen emulsions consumes about 600 -700MJ/t (2,7), which suggests that the emulsifier contributes a significant part of the global warming potential of the emulsion.

Table 1: Life Cycle Inventory for Tallowdiamine manufactured at Akzo Nobel's Stockvik, Sweden Plant (1996)

Production of 1 kg product:

Emissions into the air

CO ₂	0.6kg	Methane	0.1g
Nox	3.3g	Acrylonitrile	0.01g
Hydrocarbons	3.0g	Zinc	0.01g
CO	0.7g	HCN	0.01g
SO ₂	0.4g	Ammonia	0.01g
Particulates	0.3g	N ₂ O	0.001g

Discharges into Water

COD	19.9g	Sodium	0.06g
Sulphate	3.9g	Zinc	0.0004g
Total Nitrogen	0.8g	BOD	0.0003g
Calcium	0.2g	oil	0.0005g

Solid waste

Sludge	21.9g	Polyethylene	0.9g
Ashes	1.4g	Radioactive Waste	0.06g (from power generation in Sweden)
Mineral waste	1.5g		

Use of natural Resources

Nickel	1.1g	Bauxite	0.08g
Uranium	0.3g (from power generation in Sweden)		

3. Atmospheric emissions around cold paving operations

Microsurfacing

The levels of volatile amine compounds around a microsurfacing job undertaken by Viking Construction in Texas was determined. A latex modified cationic emulsion containing approximately 1.5% emulsifiers was used at a level of approximately 10% by weight of the aggregate which included about 0.75% cement filler. A cationic surfactant was also used as break retarder at a level of ca 0.2kg/t.

Air samples were collected from the platform immediately above the spreader box and also close to where the slurry entered the box, and represented the exposure an operator could experience.

Chipseal

The chipseal (surface dressing) operation was in upstate New York. A typical CRS-2 emulsion based on approximately 0.2% tallowdiamine. Samples were taken close to the spray bar, from inside the cab of the distributor and from in front of the chipspreader.

Analytical Method

An absorbant filter was prepared from a PTFE filter which was sandwiched between two nylon filters, then treated with a solution of tartaric acid in methanol, and dried by a nitrogen flow. Approximately 300 litres of air was pumped through at each sampling station. It was demonstrated that even at 3000liters of air no breakthrough of amines occurred. In the laboratory the amines were removed from the filter with methanol, derivatized and analyzed by liquid chromatography with uv detection. Some filters were deliberately spiked with C0 – C18 amines to act as standards. Recovery was 80-100%. The sensitivity of the method ranges from 0.05ppb (parts per billion) for low molecular weight amines like methylamine to 0.2ppb for higher amines like octadecylamine.

Results

No emulsifier was found in the air samples. From the microsurfacing operation, only ammonia and propylamine were detected at levels of ca. 20ppb and 0.15-30ppb respectively. Propylamine and ammonia are by-products of the emulsifier manufacture present as impurities in the emulsifier. Other monoamines up to C18 chain length are specifically excluded up to levels of 0.1ppb –0.2ppb.

From the chipseal operation only ammonia was detected at levels between 3 and 30ppb, depending on sampling point. The highest level was in the cab of the distributor. It probably did not come from the emulsion, but from the driver.

Conclusions

Considering that the TLV of ammonia is 20ppm (1000 times higher than the detected levels) and typical low molecular weight amines have a TLV of around 1-10ppm, atmospheric emissions of emulsifier components from cold paving operations does not seem to be an important hazard for construction workers.

4. Analysis of Run –off water and wash off water from Cold Paving Operations

In a ‘worse case’ scenario we could imagine some of the emulsifier and break control agents used in cold paving could leave in the run off water. The main concern in the case of run-off is that emulsifiers could move through the soil and eventually contaminate rivers or aquifers before they have a chance to degrade to harmless materials. The aquatic toxicity (LC-50/EC-50) of cationic emulsifiers lie in the range 0.1–10 ppm. There are therefore two issues: the concentration of emulsifier in the run-off water and mobility of any emulsifier in the soil.

Analysis of run off water from a slurry surfacing.

Run-off water from a dense-graded slurry surfacing mixture was analyzed for emulsifier by a analytical method based on Mass Spectroscopy. A slurry with a mix time of 2-3 minutes was prepared in the laboratory with following recipe:

100 g Type II aggregate

1.0 g cement
 9.0 g water
 17.0 g emulsion (1.2 % Redicote® EM26, 65% Asphalt)

Samples of “run-off” water were obtained by forming the mixture into a ball and squeezing out approximately 3 milliliters of water. The samples were taken 5, 10 and 15 minutes after mixing the ingredients.

Table 2: Analysis of Run-Off water from Slurry Surfacing

Time after mixing	Emulsifier in run-off (mg/l)	% retained
5 min	0.3	99,9996
10min	0.5	99,9993
15min	0.2	99,9997

To simulate possible leaching of emulsifier from fully or partly cured cold mixes, samples of slurry were allowed to cure 24hours or 40 days before contacting with water.

Sample 1: A slurry cake (6 mm thick) was prepared by pouring the mix in to a small polyethylene bottle and let to cure for 24 hours. 2 mm’s of water was than added on top of the slurry and let to equilibrate for 2 hours before a portion was analysed. The rest of the sample (1b) was stored for additional 40 days before it was analyzed.

Sample 2: A slurry cake was prepared and than broken in to small pieces before it was cured for 24 hours. Water was than added and analyzed after 40 days.

Sample 3: A slurry cake (6 mm thick) was made and than allowed to cured for 40 days. Water was than added to the top of the slurry (2 mm). After 20 minutes the content of the emulsifier in the water was analyzed.

	Emulsifier Content mg/l
Sample 1a, 1b	below detection limit (0,04mg/l)
Sample 2	below detection limit (0,04mg/l)
Sample 3	below detection limit (0,04mg/l)

Conclusion

Run-off water from slurry surfacing contains less than 0.5mg/l of emulsifier. Emulsifier is not leached from cured samples of slurry at levels above 0.04mg/ml.

5. Soil Adsorption Studies

Some of this work was reported at an earlier ISSA conference (8). That work showed that emulsifier was strongly adsorbed onto soils, and so even if contained in run off water, it would remain concentrated close to the road surface. Since the earlier study a more sensitive analytical techniques has been applied to the same samples. Both sets of results are shown here.

Test procedure

The initial study was carried out at the Swedish Environmental Research Institute (IVL) and an adsorption method described by the OECD was used [10]. The run-off waters were prepared by mixing CSS emulsions containing 1.2% or 1.7% Redicote EM26 (quaternary amine emulsifier) with limestone or granite open-graded aggregate mixes. The aggregates were pre-wetted with 4% water and the level of emulsion was 9%. These run off waters were diluted to approximately 10ppm Nitrogen for the adsorption studies. Three types of soil are specified in the method (see Table 2), these were used together with the two types of run-off water derived from both limestone and granite open-graded aggregates with Redicote EM26 emulsions containing two different levels of emulsifier. (12 combinations) As described in the OECD method, the soils were preconditioned by shaking for 16 hours with 10mM calcium chloride solution, then centrifuging.

The adsorption test involves conditioning the soil samples with the diluted run-off solutions by shaking for 16 hours, then centrifuging off the soils and analyzing the water phase for the residual emulsifier. The weight of soil used to treat each litre of undiluted run-off water ranges from 0.4- 5 kilos. Initial analysis was by the Kjeldahl method for total nitrogen. The results of the analysis are given in Table 4. The results from the early work shown in Table 4 indicate that 70-100% of the nitrogen content of the run-off water was adsorbed onto the soils. The relative activities of the soils were in line with earlier studies on methylamines [11]

Table 3: Variables in the soil adsorption studies

Soil Types	Emulsion	Aggregate
I (very strongly acid sandy soil)	1.2% Redicote EM26	16mm limestone
II (moderately or slightly acid loamy soil)	1.7% Redicote EM26	16mm Farsta granite
III (slightly alkaline loamy soil)		

The more accurate specific analysis measurements also shown in Table 4 suggest that practically 100% of the emulsifier is adsorbed. A possible reason of the lower estimates obtained by the nitrogen analysis method is that adsorption of emulsifier could lead to desorption of naturally occurring ammonium ions from the soil surfaces. This was supported by the data from the earlier study, which showed that when a second contact with fresh soil was made with water collected from a first contact, the result was very little further adsorption suggesting that the water at this stage contained only non- or weakly absorbing nitrogen species.

Soil samples from the adsorption tests were re-equilibrated twice with fresh calcium chloride solution and the level of nitrogen desorbed was determined.

Less than 5% of the nitrogen was desorbed in the first step and typically none desorbed in the second step, showing that once adsorbed the emulsifier is not mobile.

Table 4: Adsorption of run-off waters onto soil samples. Analysis of diluted run-off water after equilibration with soil

Run-off sample	Nitrogen content, mg/l				% Adsorbed		
	soil I	soil II	soil III		soil I	soil II	soil III
blank	0.46	<0.15	0.34				
limestone, 1.2%EM26	3.0	1.9	2.1	a	74	82	82
limestone, 1.7%EM26	2.7	1.7	1.8	a	77	84	85
granite, 1.2%EM26	2.3	0.65	0.97	a	82	94	94
granite, 1.7%EM26	1.5	0.51	1.0	a	89	95	92
granite, 1.7%EM26	1.8			c	89		
duplicates on fresh soil and run-off samples:							
blank	0.79						
limestone, 1.7%EM26	3.1			b	74		
granite, 1.7% EM26	0.85			b	99		
Data from specific analytical method							
Run-off sample	Emulsifier content mg/l				% Adsorbed		
	soil I	soil II	soil III		soil I	soil II	soil III
granite, 1.7%EM26	<0.1	<0.1	<0.1	d	>99.98	>99.98	>99.98

a) starting concentration 10mg/ml Nitrogen
c) starting concentration 12mg/ml Nitrogen

b) starting concentration 9mg/ml Nitrogen
d) starting concentration 400 mg/l emulsifier

Conclusion

Emulsifier is strongly adsorbed onto soils, and not easily desorbed.

6. Effect of soil adsorption on the aquatic toxicity of cationic emulsifiers

As a class, cationic surfactants are harmful or toxic to aquatic organisms, such as daphnia, algae and fish, when tested according to standard protocols.

We have seen that cationic surfactants are strongly adsorbed onto soils. In the standard protocols for determining the aquatic toxicity or biodegradation of chemicals, clean solutions are used without solids present. In practical situations we expect soils, humic acids and other components to be present.

Table 5 shows that the aquatic toxicity of cationic surfactant is mitigated by the presence of small amounts of humic acids such as might be expected in a natural environment.

Table 5: Effect of Humic acids on the aquatic toxicity of Cationic Surfactant (oleylamine)

	LC50 (96h) Fathead Minnow	EC50 (48h) Daphnia Magna	EC50 (growth) Algae
No Humic Acid	0.11 mg/l	0.011 mg/l	0.03 mg/l
5mg/l Humic Acids	1.50 mg/l	0.43 mg/l	0.23 mg/l
10 mg/l Humic Acids	2.13 mg/l	0.56 mg/l	0.49 mg/l

7. Conclusions

The conclusions of the various studies are that chemical emissions from slurry surfacing do not pose a significant risk to either construction workers or to the environment.

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