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Chemical Emissions from Asphalt Emulsion Applications

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Summary

At high concentrations the emulsifiers used in asphalt emulsions may pose a risk to the environment or to people. The question is whether the levels of chemicals emitted from asphalt emulsion in processes such as chipsealing, slurry seal or cold mix (fumes, run-off water) are sufficiently high to pose a significant hazard.

Cationic asphalt emulsifiers are most often amine or polyamine derivatives. Sensitive analytical techniques have been used to measure concentrations of cationic emulsifier components in the atmosphere around a microsurfacing project and in a chipsealing operation. Emulsifier was not detected in the air samples. The major amine component detected was ammonia at levels up to 20ppb (parts per billion), with minor amounts of alkylamines (0.2ppb) in the case of the microsurfacing; and undetectable amounts of alkylamines in the case of chipseal. These levels represent less than 1/1000th of the recommended exposure levels of ammonia and short chain amines. The conclusion is that workers are not exposed to dangerous levels of amines via the atmospheric route.

In a separate study, the concentrations of a quaternary amine emulsifier in run-off waters from laboratory-produced slurry seals did not exceed 0.5ppm and moreover no detectable amounts of emulsifier were found on contacting a cured seal with water, to simulate the effect of rainfall.

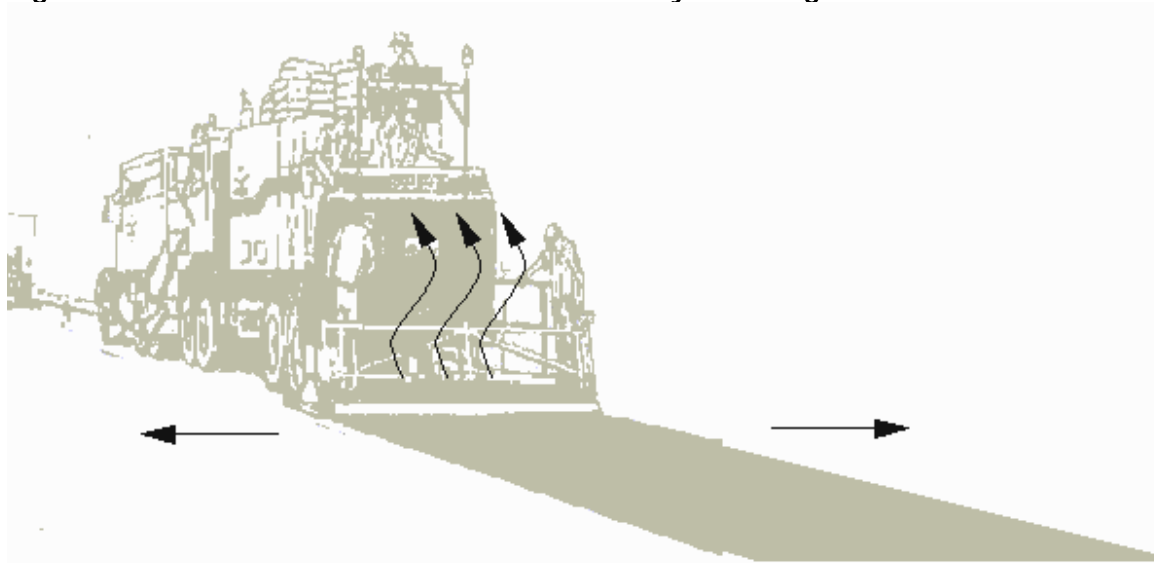
In another study, adsorption measurements of a quaternary ammonium emulsifier from run-off water onto standard soils indicated that the emulsifier is strongly adsorbed (>99.99%) and not desorbed on washing. The conclusion is that the mobility of the emulsifier in the soil environment is low - any emulsifier contained in run off or wash off water will remain close to the roadway.

Introduction

Cold manufactured road materials have environmental advantages over hot asphalt. For example their energy consumption is lower. Including transport and paving of materials, a cold constructed roadway has been calculated to use only 60-70% of the energy of a hot mixed, hot laid roadway of equivalent bearing capacity [1], and with consequent lower emissions of greenhouse gases. The hot mix process also generates fumes and particulate emissions which have to be controlled.

But what of emissions from cold paving processes using asphalt emulsions such as slurry surfacing, chipseal and cold mix? Because of the nature of the processes, these emissions are likely to be quite different from those encountered with hot mixed, hot laid materials. Slurry, for example, contains aggregate, emulsifiers, asphalt, acids, water and sometimes cement and break control additives (typically a cationic surfactant or aluminum salt). The potential emissions from the process could conceivably include volatile chemicals from the slurry entering the atmosphere and /or chemicals contained in the run-off water generated by the breaking process.

Figure 1: Possible routes of emissions from slurry surfacing



As part of the chemical industry initiative Responsible Care® Akzo Nobel is concerned about the health, safety and environmental aspects of its products in all phases of the chemical product's lifecycle including design, manufacture, distribution, use, recycling and disposal. To this end, and in cooperation with Nynas Petroleum, a company supplying both asphalt and asphalt emulsions, the fate of the asphalt emulsifier in road construction and maintenance operations has been studied.

Emulsifiers and break control additives are typically nitrogen-based cationic surfactants manufactured from natural fats and oils reacted with ammonia or polyethylenepolyamines (Figure 2) and the asphalt emulsions contain from 0.1 – 2.0% of these chemicals. These products can conceivably enter the environment by the following routes:

1. Into the atmosphere by evaporation from the laying of cold mixes like slurry surfacings, or from spray application of emulsions.
2. Contained in the run-off water occasionally seen in the laying or from stockpiles of cold mixes
3. By the washing action of rain on surface courses.

This paper reports the results of several studies designed to measure the levels of cationic emulsifiers in by each potential route and also to address the fate of the emulsifiers if they should enter the environment. Some of the data was reported earlier [2].

1. Analysis of air samples around cold paving operations

Cationic emulsifiers are high molecular weight chemicals (generally >300 daltons) with low vapour pressures which even in the undiluted state do not offer a significant inhalation risk. But it nevertheless was considered a useful exercise to actually measure the amounts of volatile amines present in field situations on the basis that it is always better to have data rather than speculation, however well-informed. The earlier study on emissions from slurry surfacing [2] showed very low values, less than 1/1000 of recommended exposure levels. This paper reports additional data for chipsealing where the emulsion is sprayed hot (50-60C).

Slurry Surfacing.

Slurry surfacing is a mixture of asphalt emulsion, water, cement and dense graded aggregate with a top size of approximately 8mm which is prepared in a mobile mix-paver and spread over the road surface.

The site was that of a microsurfacing contract undertaken by Viking Construction on Interstate 10 in Pecos County near Fort Stockton, Texas in June 1997. The weather was sunny and hot with a light wind. The latex modified CSS-1P microsurfacing emulsion was used at approximately 10% basis the aggregate. The emulsifying system was believed to contain condensates of fatty acids with polyamines as well as fatty polyamines. Cement was used at 0.75% in the slurry. 0.3-0.5lbs/ton break retarding additive similar in composition to the emulsifier was also added to the slurry on the paver.

Air samples were collected from the platform immediately over the spreader box approximately 1m above the box and also close to where the slurry entered the box and so represented the exposure than an operator on the platform could experience.

Chipseal

In chipseal an emulsion is sprayed onto the road surface, quickly covered with aggregate chippings and compacted.

The chipseal operation was in upstate New York. The CRS-2 emulsion contained approximately 0.2% tallowdiamines. Samples were taken from close to the spray bar, from inside the cab and from in front of the chipsreader.

Analytical method and Results

The collection and analytical method has been developed by Akzo Nobel's Dobbs Ferry R&D laboratories in New York. Essentially it comprises a PTFE filter pretreated with tartaric acid which traps any amines as their salts. The amines are desorbed in the laboratory, derivatized and analyzed by liquid chromatography. In the sampling procedure 75-300 litres of the air was pumped through the filter and

this procedure was carried out four times to produce four samples for analysis which were averaged. The sensitivity of the method ranges from 0.05 ppb(parts per *billion*) for low molecular weight amines like methylamine, up to 0.2ppb for higher amines like octadecylamine.

No emulsifier was found in the air samples. From the microsurfacing operation only ammonia and propylamine were detected, at levels of ca. 20ppb and 0.15-0.30ppb respectively. Other monoamines up to C18 chain length are specifically excluded up to levels of ca 0.1ppb for the low molecular weight amines and up to 0.2ppb for the higher amines.

From the chipseal operation only ammonia was detected at levels between 3 and 20ppb depending on the sampling point. Interestingly, the highest concentration was from inside the cab.

2. Analysis of run-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. Emulsifiers are biodegradable. 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) 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 1: 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

In these cases more than 99,99% of emulsifier was adsorbed in the seal and the run-off water contained less than 0.5 mg/l of emulsifier.

3. Soil Adsorption Studies

An earlier study [2] indicated that even if emulsifier was contained in run-off water it was strongly adsorbed onto soils and so remained close to the roadway. But the analytical method used in the earlier study was a non-specific. It was based on Nitrogen content and the interpretation was complicated by the fact that the aggregate, asphalt and the soils also contained nitrogen. This paper reports an extension of the work where some samples have been re-analyzed by a sensitive Mass Spectroscopy technique, specific to the emulsifier so allowing an unequivocal interpretation.

Test procedure

The initial study [2] was carried out at the Swedish Environmental Research Institute (IVL) and an adsorption method described by the OECD was used [3]. 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 saturating with 10mM calcium chloride solution by shaking for 16 hours, 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 liter of undiluted run-off water ranges from 0.4- 5 kilos. Initial analysis was by Kejdahl for total nitrogen. The results of the analysis are given in Table 3. The results from reference [2] shown in Table 3 indicate that 70-100% of the nitrogen content of the run-off water was adsorbed onto the soils.

Table 2: 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 3 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. The relative activities of the soils were in line with earlier studies on methylamines [4]

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 3: 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

4. Analysis of wash waters

The fully cured cold paved roadway contains the emulsifiers from the emulsion used to construct the roadway. Indeed these emulsifiers probably provide an antistripping effect in the mixture. The question is – can they be extracted by rainfall? In order to simulate the effect of rain on the partly and fully cured slurry surfacing, samples were subjected to contact with water. The curing process is a

gradual one and as it progresses the emulsifier may become more and more immobilized in the asphalt mixture, so samples were prepared after different curing times.

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)

In all cases no emulsifier was detected in the water samples indicating that the emulsifier rapidly becomes immobilized in the asphalt layer and that washing off by rainfall does not lead to significant concentrations of emulsifier.

Discussion

The atmospheric measurements confirm that no significant levels of emulsifiers and emulsifier components are emitted into the air above cold paving.

The emulsifier itself was not detected because of the low volatility of the high molecular weight emulsifier active components. What were detected were extremely low concentrations of volatile amines probably present as impurities in the emulsifier and /or the other components of the slurry or chipseal.

To put the results into perspective, the recommended 8 hour time weighted average personal exposure limit to ammonia is 25ppm, some 1000 times higher than was detected immediately above the spreader box. Similarly, the exposure limits for low molecular weight amines are typically in the range 0.5-10ppm some 3000-50000 times higher than that detected directly over the spreader box.

The measurements on run off water show that in the dense graded slurry surfacing > 99,99% of the emulsifier was adsorbed in the mix. The levels of emulsifier in the

run-off water were approximately 0.5ppm, which allowing for dilution would not threaten aquatic organisms even if added directly to a watercourse. The evidence from the soil adsorption studies was that emulsifier in the run-off water is in any case almost completely (>99.9%) adsorbed onto soil and, once adsorbed, is difficult to desorb.

Leaching or wash off of emulsifier from the cured mix is not significant.

Conclusions

Atmospheric emissions of amines from slurry surfacing and chipseal operations are at least a thousand times lower than occupational exposure limits and in the case of organic amines are close to or lower than the limits of detection.

Emulsifier in run-off water is low in the case of dense-graded mixtures and is almost completely adsorbed by soil close to the roadway.

References

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