

Chemical Emissions from Slurry Surfacing

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Summary

Slurry surfacing contains chemicals such as emulsifier, break control additive, acids and bases as well as Portland cement or hydrated lime. At high concentrations some of these chemicals may pose a risk to the environment or to workers. The question is whether the low levels of chemicals emitted from the slurry process (fumes, run-off water) pose a significant hazard.

Slurry emulsifiers are most often amine or polyamine derivatives. Emissions of volatile amine components from a microsurfacing project in Texas have been measured by a particularly sensitive analytical technique. The major component detected was ammonia at approximately 20 ppb (parts per billion), with minor amounts of alkylamines (0.2 ppb). 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.

Adsorption studies of a quaternary ammonium emulsifier from run-off water onto standard soils indicate that the emulsifier is strongly adsorbed 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.

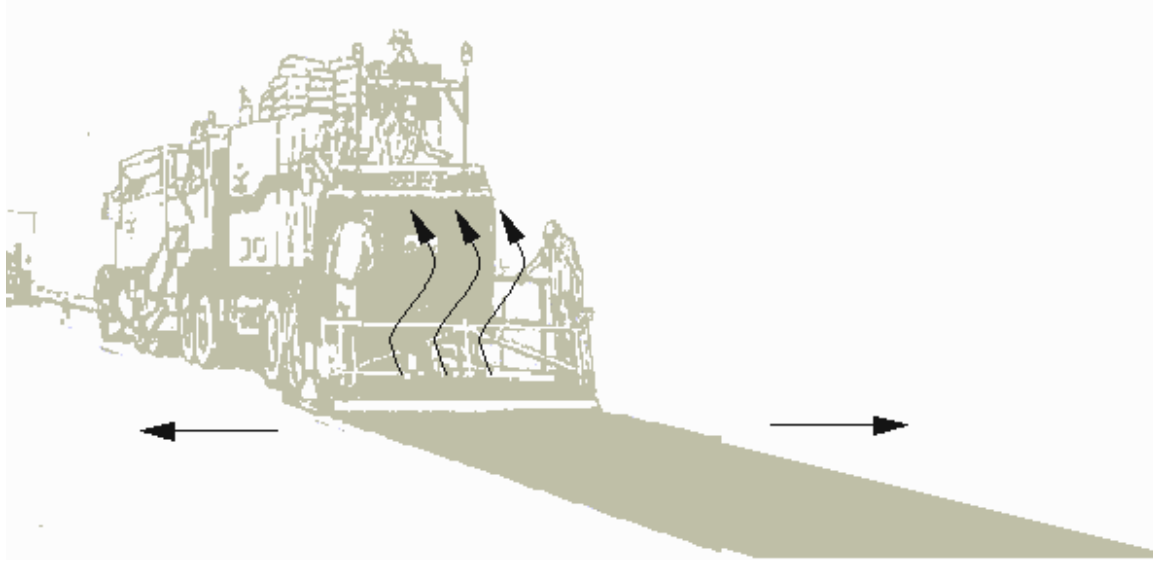
Introduction

Cold mixed 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]. The hot mix process also generates fumes and particulate emissions which have to be controlled.

But what of emissions from cold paving processes such as slurry surfacing? Because of the nature of the process, these emissions are likely to be quite different from those encountered with hot mixed, hot laid materials. Slurry 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

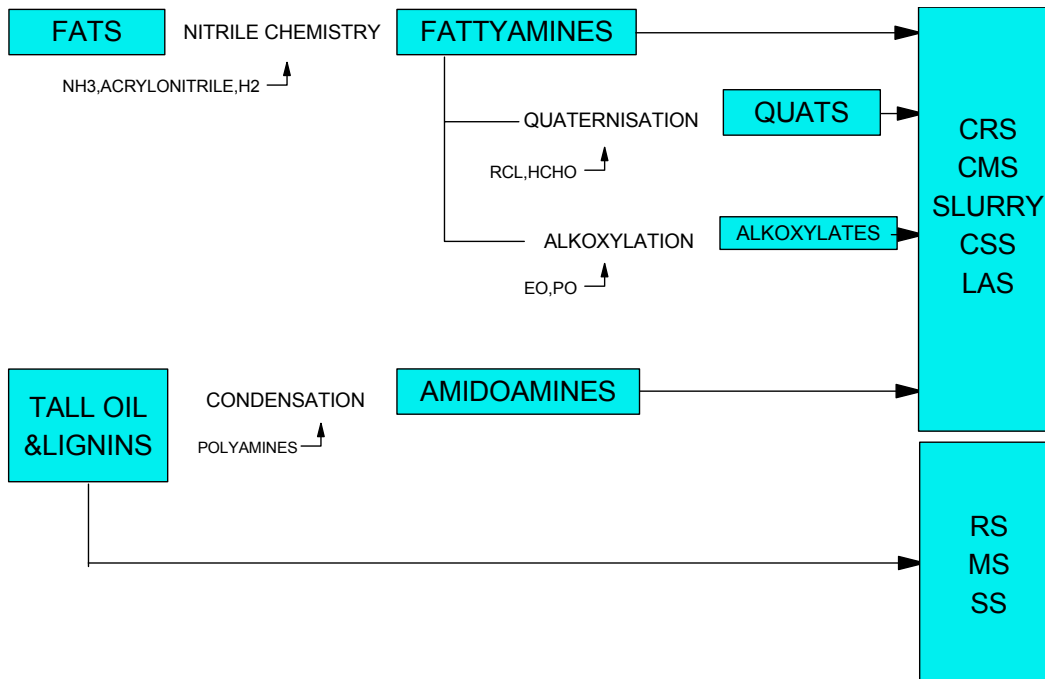


In this study we have concentrated on the emissions derived from the emulsifiers and break control additives present in the slurry. These emulsifiers are typically cationic surfactants manufactured from natural fats and oils reacted with ammonia or polyethylenepolyamines. In this study we have measured the levels of volatile amines emitted from the slurry into the atmosphere and the fate of any emulsifiers present in the run-off water.

Cationic emulsifiers are high molecular weight surfactants with low vapor pressures which even in the undiluted state do not offer a significant inhalation risk. Nevertheless, it was considered a useful exercise to measure the amounts of volatile amines present in a real-life field situation on the basis that it is always better to have data rather than speculation, however well-informed. A similar study on the emissions of volatile amines from hot mix containing amine antistrips showed very low values [2].

Previous work has indicated that the level of emulsifiers in run-off water is very low, but in a 'worst case' scenario we could imagine some of the emulsifier and break control agents could leave in the run-off water. Some of the cationic emulsifiers have fish toxicities in the range of 0.1-1 ppm, others in the range 1-10 ppm. The main concern in the case of run-off is that emulsifiers could move through the soil and eventually contaminate rivers or aquifers before having a chance to degrade to harmless materials. This study focussed on the fate of any surfactant which did run off the roadway into the surrounding soil by looking at the adsorption and desorption of emulsifiers from run-off onto typical soil samples. Strong adsorption of emulsifier would essentially immobilize any chemicals close to the roadway until they degraded.

Figure 2: Main routes to the manufacture of asphalt chemicals



Atmospheric measurements

Collection and analysis of samples.

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. 0.3-0.5 lbs/ton break retarding additive (amidoamine) was used as well as the latex modified microsurfacing emulsion (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 microsurfacing.

Air samples were collected from the platform approximately 1m above the spreader box and also close to where the slurry entered the box. These samples represent the exposure that an operator on the platform could experience.

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 approximately 300 liters of 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 for low molecular weight amines like methylamine up to 0.2 ppb for higher amines like octadecylamine.

Results of analysis of atmospheric samples

Only ammonia and propylamine were detected, at levels of ca. 20 ppb and 0.15-0.30 ppb respectively. Other monoamines up to C₁₈ chain length are specifically excluded up to levels of ca. 0.1 ppb for the low molecular weight amines and up to 0.2 ppb for the higher amines.

Soil adsorption studies

Test procedure

The study was jointly funded by Akzo Nobel and Nynas Petroleum and was carried out at the Swedish Environmental Research Institute (IVL) under the management of Osten Ekengren and their report forms the basis of the results presented here. The focus of the work was run-off from cold mixed materials in general, not specifically slurry surfacing. To provide samples of run-off water an open-graded mix design was selected since this both made it easy to collect the run-off water and provided a 'worst case' scenario because the low surface area of the aggregate will retain less emulsifier. The levels of emulsifier in the run-off water from the dense graded slurry surfacing are likely to be very much lower.

The adsorption method used specifically excludes insoluble materials and so a totally water-soluble CSS emulsifier Redicote EM26 was selected. This emulsifier is typically used in slurry applications and semi-dense cold mixes but was perhaps a little 'slow' for the open graded mix used to generate the run-off water. The result was that the run-off water also contained some bitumen.

An adsorption method described by the OECD was used [3]. Three types of soil are specified in the method (see Table 1); these were used together with two types of run-off water derived from both limestone and granite 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 with 10mM calcium chloride solution for 16 hours and then centrifuging. This calcium chloride solution was used to dilute the test solutions of emulsifiers.

The run-off water samples were prepared from laboratory mixes with either limestone or granite aggregates (see below). 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 residual emulsifier. Analysis was by the Kjeldahl method for total nitrogen. This method is not specific to the emulsifier, since the bitumen and the soils also contain some nitrogen. A blank experiment with no emulsion was also performed.

Table 1: 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)		

To simulate the effect of the movement of run-off water through the soil, a further adsorption test was done on the water recovered from the first tests. The aim was to see if further adsorption would occur, or whether this solution contained only non-adsorbing compounds.

Desorption tests were performed on only one soil, using freshly prepared samples of run-off water. The desorption test involved shaking the soil (containing adsorbed emulsifier) twice with a solution of calcium chloride and centrifuging at each stage. The aim was to see how tightly the emulsifier was bound to the soil.

Analysis of the run-off water

The run-off waters were prepared by mixing CSS emulsions containing Redicote EM26 at levels of 1.2% or 1.7% with two different aggregate mixes (either limestone or granite). The aggregates were pre-wetted with 4% water and the level of emulsion was 9%. The analysis of the run-off waters is shown in Table 2. Bitumen contains a small amount of nitrogen (ca. 0.4%) and some of the nitrogen in the run-off water may be derived from the bitumen droplets, which could be seen in some of the samples. Evaporation of the run-off samples and analysis of the organic matter recovered (4% by weight) gave a nitrogen content of 0.64% compared to 2.8% for the emulsifier and 0.4% for the bitumen. This suggests that the organics contain about 90% bitumen and 10% emulsifier and consequently about 40% of the nitrogen values shown in the table are derived from the emulsifier, 60% from the bitumen.

The emulsions had a nitrogen content of ca. 3000 mg/l, so the level of nitrogen (emulsifier plus bitumen) has been reduced by 90-98% in the run-off water. If only bitumen had been retained in the mix and all the emulsifier had passed through together with the water phase and pre-wet water, then we could expect up to ca. 500-700 mg/l nitrogen in the run-off water. If we accept that about 40% of the nitrogen contents shown in Table 2 are derived from the emulsifier then we can calculate that about 80-95% of the emulsifier is retained in the cold mix.

Table 2: Analysis of run-off waters from open-graded emulsion mixes

Aggregate	Emulsion	Nitrogen (mg/l)
limestone	1.2% Redicote EM26	47
limestone	1.7% Redicote EM26	67

limestone	1.7%	Redicote EM26	37 ^a
granite	1.2%	Redicote EM26	178
granite	1.7%	Redicote EM26	262
granite	1.7%	Redicote EM26	230 ^a

a) duplicate preparation

Adsorption from run-off water onto soil samples.

The run-off samples were diluted to 9-12 mg/l nitrogen with calcium chloride solution and the adsorption test with the three soil samples was carried out. The dilution was carried out because it was required in the test protocol to ensure the correct ratio of soil to chemical, but was limited to 10 ppm because of the sensitivity of the analytical method. Since we are interested in the ultimate concentration of nitrogen reached in the water phase after passage through the soil, the dilution is not critical. The weight of soil used to treat each liter of undiluted run-off water ranges from 0.4-5 kilos. The results are shown in Table 3.

The soil samples themselves contain some soluble nitrogen which is extracted into the calcium chloride solution during saturation of the soils, so even the blank determinations (no run-off water) contain nitrogen. These values were used to correct the values for the test samples and the percentages of nitrogen adsorbed were calculated.

Soil I has a lower affinity for the nitrogen-containing compounds than soils II and III, probably because of its lower clay content and in line with previous studies on the adsorption of methylamines and other low molecular weight amines on these soils [4]. It appears that the run-off water from the limestone aggregate showed somewhat less reaction with the soils than run-off water from the granite.

Taking all the results together, between 70 and 100 percent of the nitrogen in the run-off water has been adsorbed.

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.

**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		

a) starting concentration 10mg/l nitrogen
c) starting concentration 12mg/l nitrogen

b) starting concentration 9mg/l nitrogen

Desorption of nitrogen from soil

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.

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.

To put the results into perspective, the recommended 8 hour time weighted average personal exposure limit to ammonia is 25 ppm, 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 0.5-10 ppm, some 3000-50,000 times higher than that detected directly over the spreader box.

The measurements on run-off water are more complicated to interpret because of the non-specific analytical method used. It was not possible to separate nitrogen compounds derived from the bitumen and those from the emulsifier. It is even possible that some inorganic nitrogen was present in the aggregates used to generate the run-off water. It must also be remembered that the study was made with an open graded mix so that the absolute levels of emulsifier in the run-

off water are considerably higher than would be found in slurry surfacing. Even so more than 80% of the emulsifier was retained in the mix itself.

The results provide a worst case limit on the amounts of emulsifier which are not adsorbed. Between 75 and 100% of any nitrogen (derived from the bitumen and emulsifier) present in the run-off water is adsorbed more or less irreversibly on the soil. The nitrogen-containing materials remaining after soil contact are not adsorbed even after repeated contact with fresh soil which indicates that these materials are probably not the emulsifier itself.

Because of the nature of the test protocol it was not possible to work with some of the more usual slurry emulsifiers and we are studying how to modify the procedure. A more specific and sensitive analytical technique will be required to eliminate the uncertainties in the present study.

Conclusions

Atmospheric emissions of amines from slurry surfacing 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 largely adsorbed by soil close to the roadway.

Acknowledgements

Our thanks to Dr. W. Joyce of Akzo Nobel Dobbs Ferry for developing the analytical methods used and for performing the analytical work on the air samples.

References

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