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Technical Report

Nitrosamines and Other Hazardous Emissions From Engine Crankcases

by

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I. Background

Under most operating conditions, the crankcases of automotive engines emit a stream of effluent composed of gases and particulate matter. Most of the gaseous portion of this effluent stream originates at the imperfect seal of the piston against the cylinder wall. This "blowby" originates in the combustion chamber and, after "blowing by" the piston rings, enters the crankcase and is then vented. A large part of the particulate matter in the crankcase effluent stream appears to originate in the crankcase.

The crankcases of all gasoline fueled engines were subjected to regulatory control in 1968. This regulation prohibited any crankcase emissions from gasoline fueled light duty engines and resulted in the use of total recirculation of these emissions through the engine. Since that time, crankcase emissions have been prohibited from light duty gasoline engines and are currently prohibited by CFR 86.081-8 (c) (reference No. 1)*. For light duty gasoline trucks, crankcase emissions are prohibited by CFR 86.081-9 (c) (reference 1), and for heavy duty gasoline engines by CFR 86.080-10(c) (reference 1). At the time the first gasoline engine emissions control regulations were promulgated, it was determined that Diesel crankcase emissions did not need to be so regulated because of their low HC, CO, and NOx content. For many years most light duty Diesels have used crankcase emissions recirculation. Recently, however, some light duty Diesel manufacturers have eliminated crankcase controls. Until recently, almost no heavy duty Diesel engines employed crankcase controls, but rather discharged the effluent into the atmosphere. This situation will change in 1984 when CFR 86.084 - 11 (c) (reference 1) takes effect. This will require crankcase effluent control on heavy duty naturally aspirated Diesel engines but not on turbocharged or Roots supercharged Diesel engines. Therefore, most bus engines would be permitted to exhaust their crankcase effluent into the atomosphere. In fact, since most heavy duty Diesel engines are expected to be turbocharged, most of these engines will also have no mandated crankcase control. The gas phase portion of the crankcase stream contains pollutants such as HC, CO, NOx, aldehydes and other gases. These exist at levels of 0.005 to 4.1 percent of the corresponding exhaust emissions (e.g., crankcase emission levels of HC are about 0.2 to 4.1 percent of the HC exhaust emission levels) (2). The gas phase also contains nitrosamines, a very strong carcinogen(8). These are emitted at levels up to 268.8 µg/hour (3).

* Number in parenthesis identifies the reference, a list of which is found at the end of the paper.

The particulate portion of the Diesel crankcase effluent stream consists primarily of heavy hydrocarbons. About 88% to 98% of this material is solvent-soluble organic matter with the remainder being carbonaceous particulate and a small amount of sulfate. Analysis of this particulate indicates that the soluble portion is largely a lubricating oil-type of material which leads one to conclude that it could be entrained lubricating oil mist material (3). Fresh lubricating oil appears to be biologically benign (4), but used lubricating oils have been known to be a carcinogen since 1935 (5). More recent work has shown used lubricating oils to be mutagenic, also (4, 6).

II. Nitrosamine Emissions

Nitrosamines are a group of compounds that take the general form of $R_2N = NO$ (7). Lijinsky (8) has described them as follows:

> "Among carcinogens the N-nitroso compounds are the most broadly acting and among the most potent. They comprise the directly acting nitrosamides and the systematically acting nitrosamines, which require enzymic activation for their carcinogenic action.-------More than a hundred N-nitroso compounds have been tested for carcinogenic activity and most of them have induced tumors in rats; a much smaller number has been tested in hamsters, mice or guinea pigs and, again, most of those tested have been carcinogenic."

In recent testing of Diesel crankcase emissions, nitrosamines were found to be present in all of the samples taken (3). The nitrosamine levels appeared to be a function of the lubricating oil used (brand and age), the engine and its associated crankcase NOx flow rate, engine operating cycle, and possibly other factors not addressed by the experimental design.

The major influence on Diesel crankcase nitrosamine emissions appears to be the lubricating oil. All engine lubricating oils contain an additive package designed to help the oil function better in high pressure areas, to suspend foreign matter, to widen the viscosity range and to prevent rapid deterioration by oxidants and acids. Many of these additives contain amines and other nitrogen-containing compounds. The research described in references 3 and 9 indicated that the interaction between these nitrogen-containing oil additive compounds and the crankcase NOx and elevated temperatures resulted in the formation of nitrosamines.

Reference (3) indicated that there are large differences in the amount of nitrosamines that result from the use of various oils. In order to quantify this effect, a bench procedure was developed to determine the nitrosation potential associated with a given oil. This yielded much interesting data. For example, base oil (before the additive package is added) has no ability to form nitrosamines under this procedure. However, 84% of the 62 samples of fresh oil that were analyzed for their nitrosation potential yielded dimethylnitrosamine (NDMA). Of the 60 fresh oils that were analyzed for their nitrosation potential, 38% yielded n-nitrosomorpholene (NMOR). (Few of these oil samples had detectable levels of nitrosamines before artificial nitrosation.)

The nitrosation potential for NDMA of fresh oils ranged from a low of 0.6 ppb to a high of 202 ppb; a range of 337 fold, dividing the highest by the lowest. Thus, there is a large difference in the ability of different brands of oils to form nitrosamines. There is also a difference in nitrosation potential of a given brand of oil. For example, Amoco 300 SAE 30 from the Whiting refinery has a much higher nitrosation potential than the Amoco 300 SAE 30 from the Houston refinery because of different levels of additive required at the two refineries.

Given that there is a wide difference in the ability of different oils to form nitrosamines, it would follow that the nitrosamine emissions from a given engine's crankcase would vary as a function of the oil. This, as it turns out, was the case in the experimentation described in reference 3. A single heavy duty Diesel engine (Mack ETAY(B) 673A) was tested with four different oils representing a range of different nitrosation potentials as measured by the bench procedure. The results are presented in Table 1 and they showed a very clear correlation (r=0.97) between nitrosation potential and nitrosamine emissions.

Table 1

Table of NDMA in Nitrosated Oil Vs. Average NDMA in Crankcase Emissions For Mack ETAY(B) 673A HD Diesel Engine

Oil	NDMA in Nitrosated Oil (ppb)	Average* NDMA Emission Rate (ug/hr)
Shell Rotella T (SAE30)	1	4
Amoco 300 (SAE30)	25	36
Mobil Delvac 1200 (SAE30)	88	96
Mobil Delvac Super (15W40)	200	144

* Average of two measurements per mode. The seven modal averages are then composited using distributed weighting factors based on 13 mode weighting factors.

The measurements for the data presented in Table 1 were taken after one hour of preconditioning on the fresh oil so that experimental consistency could be maintained. Therefore, the results are valid only for the fresh oil case. Nevertheless, there appears to be some influence due to the age of the oil on the nitrosation potential of the oil and the associated nitrosamine emissions. Some heavy duty Diesel engine manufacturers supplied oils for nitrosamine and nitrosation testing from in-use engines. These samples included a fresh sample and samples taken at various in-use intervals. Un-

fortunately, most of the oils chosen had low fresh oil nitrosation potentials. The results showed that of the eight used-oil series tested, all but two of them had declining (or no detectable) nitrosation potential levels. On the other hand, some extended mileage samples taken from the various vehicles showed significant levels of nitrosamines. Therefore, it must be concluded that the ability of an oil to form nitrosamines probably decreases with time of use. The rate at which this decrease occurs has not been quantified. This change in the ability of the oil to form nitrosamines may be related to the consumption or deterioration of the additive package.

The type of engine also has an effect on the nitrosamine levels emitted. Reference 3 describes the results of nitrosamine emissions measurements taken from three different engines operated on one type of oil. These results are presented in Table 2. References 3 and 9 conclude that the engine variables primarily responsible for the variation in nitrosamine levels shown in Table 2 are 1) crankcase flow rate of NO and NO_2, and 2) volume flow rate of crankcase gases which influences residence time of NOx with the nitrosatable amines.

Table 2

Table of Nitrosamine Emission Rates of Four Different Engines Operated on Mobile Delvac Super (15W40)

	NDMA Emission Rate, ug/hr	
Engine	Peak	Weighted@ Composite
Mack ETAY (B) 673A	268.8	135.4
DDAD 6V-71 N	52.2	11.0
Caterpillar 3406	71.2	35.8
Mercedes 240D*	18.4	13.8

* Light Duty Vehicle. Data in "Weighted Composite" Column are Geometric Average of 2 Steady State Modes.
@ 7 mode composite - see footnote, Table 1

The impact that these emission levels has on ambient air nitrosamine levels is not a straight forward issue to analyze. Such an analysis is complicated by lack of a crankcase emissions dispersion model. However, some data can be discussed in this regard.

Very little monitoring of roadside nitrosamines has been performed. The limited amount of monitoring performed to date has shown levels in the range of 1 $\mu g/m^3$. For example, Gordon (10) sampled air along roadways in the Los Angeles basin and found levels up to 1.1 $\mu g/m^3$. He found no evidence for any specific point emission sources for the nitrosamines. He found peak levels at about 8 am and 6 pm. He feels that there is a high likelihood that the source is mobile source related (11).

Shapley reports levels of NDMA of 0.8 $\mu g/m^3$ on the Cross-Bronx Expressway in New York City (12) and infers that this is probably mobile source related but could not identify a specific mobile source for this finding. Pellizzari (13) reported 0.1 ppb of diethylnitrosamine as well as DMNA in the Eisenhower Tunnel in Colorado. This is also probably mobile source related since the tunnel is an area away from industry and since it is a motor vehicle tunnel.

As far as sources of this nitrosamine are concerned, few such sources are confirmed except for crankcases. Some data was reported by Urban, et al.. (14) which were in the form of mass spectroscopy results at the same retention time as NDMA. These were taken from various vehicles equipped without catalysts and with oxidation catalysts. The data are considered to be inconclusive evidence of nitrosamine presence in gasoline fueled vehicle exhaust. GM has also presented data that can be considered to be inconclusive with respect to the identification of nitrosamines in gasoline fueled vehicle exhaust (15).

Cadle et al.. (16) report results of work done in search for amines (nitrosamine precursors), under the theory that such amines may react with nitrous acid in the atmosphere to form nitrosamines. Their conclusion is that "it is unlikely that any of the standard gasoline cars on the road today are emitting significant quantities of amines" and therefore little liklihood of gasoline fueled cars contributing significantly to the nitrosamine levels reported. Also, Hurn et al.. (17) could not detect amines in the exhaust of noncatalyst cars. Consequently, it appears one could conclude that there is little data that show that exhaust from gasoline fueled engines (light or heavy duty) contributes to roadside nitrosamine levels.

Currently, there are only two confirmed sources of mobile source nitrosamines and one strong indication of mobile source nitrosamines. The confirmed sources are crankcase emissions from Diesel engines and vehicle interior emissions (18, 19). The strong indication of nitrosamines in exhaust is reported in reference 3. While performing engine sampling for crankcase nitrosamines, raw exhaust emissions were sampled from one of the heavy duty Diesel engines. The results of this showed emission rates of about 13.6 $\mu g/min$. The method used was one that was qualified for crankcase emissions (i.e., a high NOx environment) but not specifically for raw engine exhaust. Therefore, the results should be considered as strongly indicative of the presence of NDMA, but not as confirmed evidence. Very recent work

being performed at Southwest Research Institute (20) has shown no exhaust nitrosamines from a light duty Diesel engine (Fiat, naturally aspirated) using a qualified methodology. How this result impacts the heavy duty Diesel engine result is not known.

How do these confirmed sources of NDMA contribute to the NDMA levels found along roadways? This is a question which is not very easy to answer. The data indicate that crankcase emissions contain NDMA at concentrations up to 28 ug/m^3 (3). Roadway concentrations up to 1.1 ug/m^3 have been detected. What portion of the roadside level is contributed by crankcase emissions? No really adequate dispersion model currently exists to compute this. One way to approximate this might be to ratio the numbers that were used in the support documentation for the Heavy Duty Particulate rulemaking (21). Such an approach yields a NDMA concentration of 19×10^{-12} g/m^3 from crankcases; a small fraction of the 1.1×10^{-6} g/m^3 NDMA observed along roadways.

If the same method (21) were to be used for the tentative Diesel exhaust NDMA emission factor, the result would be $112 \times 10^{-12} g/m^3$, again a small fraction of the observed roadway concentrations.

Another approach would be to look at the relative hazard assoicated with the levels of nitrosamines observed along roadways. Assume a roadway concentration of 1.1 ug/m^3 of NDMA (of which the crankcase emissions would contribute a part) and also postulate a hypothetical commuter spending 2 hours per day breathing such air (which can be a relatively conservative assumption). At a 10 liters/min respiration rate and an assumed total pulmonary adsorption of the NDMA, this person would intake

$$(1.1\ ug/m^3)\ (10\ l/min)\ (0.001\ m^3/l)\ (2\ hr)(60 min/hr) = 1.3\ ug\ NDMA.$$

This is about equivalent to the nitrosamine level of one can of beer or several strips of bacon (22). Obviously, the amount of nitrosamine intake would increase with increasing exposure. Also, this exposure would also add to any exposure from the interior of the automobile. Using the EPA risk assessment model (23)which is used for drinking water risk assessment, this would translate into an cancer incidence of 0.36 per 100,000 populaton per year. Assuming 150 million Americans are so exposed, the number of annual cancer incidents attributable to roadside DMNA concentrations of 1.1 ug/m^3 would be 546. However, as Fine points out (23):

> "The animal data base for the low dose response study is based on the 1963 study of Druckrey. Very recent work in England has found that NDMA causes increased tumor incidence in rats at a level of 0.035 - 0.130 ug/l, which is 10 to 30 times less than the earlier Druckrey study. If the latest British data had been used to calculate the risk assessment, the number of incidents would have been increased 10 to 30 fold."

If one assumes a 20 fold increase in incidents due to more up to date potency data, this would result in 10,920 incidents of cancer per year due to roadside nitrosamines. If one were to assume only 1.5 million persons (0.68% of the total U.S. population) were exposed to the 1.1 $\mu g/m^3$ levels, the number of of cancer incidents would then be 109 per year.

The other confirmed source of nitrosamines is automobile interiors. The work by Fine et al.. (18, 22) has shown levels in new automobiles as high as 0.83 ug/m^3. The work done recently by Smith (19) for EPA (ECTD) found a maximum level of 0.63 $\mu g/m^3$. This level decreases with vehicle operation to about one fifth of the at-rest concentration, or 0.13 ug/m^3 when applied to his maximum concentration. Using the same assumptions as above, a hypothetical commuter traveling for 2 hours per day (with 10 min/day at the at-rest concentration) would be exposed to 0.21 ug of NDMA. Using the up to date potency data for NDMA and assuming only 0.68% of the population is so exposed, 21 additional incidents per year of cancer would occur.

The crankcase emissions from a light duty Diesel engine were sampled and a nitrosamine (NDMA) emission rate of 18.4 ug/hr (9.2 $\mu g/m^3$) was determined for a 50 mph steady state condition. Therefore, light duty Diesel crankcase emissions will also contribute to roadside nitrosamine emissions if they are emitted into the atmosphere. Currently, most such vehicles have crankcase gas recirculation systems. However, some are being equipped with road draft tubes to vent the crankcase to atmosphere.

No nitrosamine measurements have been taken of gasoline crankcase exhaust because of regulations prohibiting crankcase venting to atmosphere (1). However, from the available evidence (3), it can be concluded that such engines would probably contribute even more nitrosamines to ambient levels because oils designed for use in gasoline engines usually contain more of the amine containing compounds. This is verified by bench nitrosation of used gasoline-fueled-engine oils which usually show positive levels of nitrosamines.

III. Particulate

The effluent stream from Diesel engine crankcases is composed of particulate matter as well as gases. Table 3 gives some particulate data from several engines. The particulate emissions are primarily composed of soluble organic matter, and the indications are that it is mostly of a lubricating oil nature (2). Therefore, most of the particulate may be entrained lubricating oil.

Table 3

Table of Particulate and BaP Rates for
Three Heavy Duty Diesel Engines (2)

Engine	Particulate* Mass Rate, g/hr	Percent Solubles	BaP, ug/hr	Weight % BaP in Particulate
DDAD 6V-71	0.80	88.2	25.0	0.0031
DDAD 6V-71	2.44	98.1	76.8	0.0032
Cummins NTC-350	1.01	93.0	10.2	0.00094

* 7 mode composite

Also, the data in Table 3 show that the particulate contains benzo-a-pyrene, which is emitted at a rate of from 10 to 77 µg/hr.

Again, it would be useful to know what hazard, if any, these particulate emissions represent. The benzo-a-pyrene is well known to be a carcinogen, one that does require metabolic activation. Used lubricating oil itself has been known since 1935 to be a carcinogen. Twort et al.. (5) has reported used lubricating oils as being carcinogenic as determined by mouse skin painting. They observed that used oils are more carcinogenic than fresh oils. More recent work done by Wang et al..(4) has shown that unused motor oil samples were not mutagenic but that motor oil from a CFR single cyclinder engine became mutagenic after 43 hours of running. All mutagenic measures were made by the Ames test, strain TA98. Payne et al.. (6) has also reported the mutagenic nature of used crankcase oils, both neat and fractionated. Payne also reports (24) that mutagens (some of them possibly very potent) are found in nitrosated samples of petroleum. Finally, there is some indication that used lubricating oil can contain some polychlorinated biphenyls (PCBs) which are known to be carcinogenic.

IV. Summary and Conclusions

The emissions from heavy duty Diesel crankcases contain a number of hazardous compounds. Research has discovered some of them and it may be possible that there are some that have not yet been quantified. Nitrosamines (a potent carcinogen in animals and probably also in humans) are emitted from engines using fresh oil. These emissions seem to be a function of the type of oil used and some engine parameters such as crankcase flow rate of NOx compounds. There is some evidence that the emission rate of nitrosamines may decrease with time, but this has not been thoroughly investigated. It is currently difficult to convert the nitrosamine emission rates into roadside concentrations due to lack of a model tailored especially for that purpose. The observed roadside concentrations are quite significant and could possibly contribute to several hundred cases of cancer per year. The only confirmed sources of this nitrosamines are Diesel crankcases and automobile interiors. Diesel exhaust is also a possible source. Spark ignition engines are probably not a source of either nitrosamines or nitrosamine precursors (ie., amines). Other exposure scenarios for nitrosamines should be analyzed, such as tunnels, garages, bus terminals, etc. The role of crankcase emissions should be analyzed when evaluating epidimiological data taken from such confined areas. The highest priority seems to be acquiring some more roadside nitrosamine measurments to confirm the limited data available. Work is also needed to determine the atmospheric fate and reactions of nitrosamine (e.g. would nitrosamines emitted by roadsides have a long atmospheric life and widely diffuse into the urban air?).

The particulate emissions from Diesel crankcases contain what appears to be mostly entrained lubricating oil. Used lubricating oil has been shown to contain carcinogenic compounds such as benzo-a-pyrene. It has also been shown to be carcinogenic when tested in skin painting experiments. It has also been shown to be mutagenic, both neat and fractionated. Therefore, it can be concluded that the particulate portion of the crankcase effluent stream may start out after an oil change at a level containing few carcinogenic compounds but the level of these compounds increases with time. In summary, crankcases emit a variety of hazardous chemicals and evaluation of the costs and benefits of the control of these emissions should be seriously considered.

References

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From Table 1, the Heavy Duty Diesel Truck (HDT-D) emission factor is 2.0 g/mi and the HDT-D VMT represents 25% of the total VMT. Combining these, the HDT-D represents 40% of the total weighted emission factor used. This weighted emission factor was used to compute ambient particulate concentrations from Diesel HD truck. Taking the ratio of the HDT-D portion of the total resultant ambient concentration to the HDT-D emission factor and then multiplying by the HDT-D nitrosamine emission factor, the ambient nitrosamine concentration is computed. The exhaust nitrosamine emission factor is used in the same manner to compute the exhaust contribution to ambient nitrosamine concentrations.

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