State of California
California Environmental Protection Agency

STAFF REPORT

Multimedia Evaluation of Viscon-Treated Diesel Fuel

June 2011

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Acknowledgements

The multimedia evaluation of Viscon-treated diesel fuel was conducted by the Multimedia Working Group with the assistance and support of other individuals within the California Environmental Protection Agency and academia.

We recognize the dedication and expertise of the late Bruce Winder, who provided significant contributions to this evaluation. Thank you, Bruce.

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GLOSSARY

ARB	Air Resources Board
Cal/EPA	California Environmental Protection Agency
CCR	California Code of Regulations
CEPC	California Environmental Policy Council
DECS	Diesel Emission Control Strategy
DRI	Desert Research Institute
DTSC	Department of Toxic Substance Control
CO	Carbon Monoxide
CO2	Carbon Dioxide
GC	Gas Chromatography
HP	Horsepower
HS&C	Health and Safety Code
MMWG	Multimedia Working Group
NMHC	Non-Methane Hydrocarbons
NOx	Oxides of Nitrogen
OEHHA	Office of Environmental Health Hazard Assessment
Olson Lab	Olson Ecologic Engine Testing Laboratories
PAHs	Poly Aromatic Hydrocarbons
PIB	Polyisobutylene
PM	Particulate Matter
SWRCB	State Water Resource Control Board
TAC	Toxic Air Containment
THC	Total Hydrocarbons
UHMW	Ultra-High-Molecular-Weight
ULSD	Ultra-Low-Sulfur-Diesel
UST	Underground Storage Tanks
VOC	Volatile Organic Compounds

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I. Introduction

Viscon California, LLC applied for verification of its proprietary fuel additive, Viscon®, in accordance with the Air Resources Board (ARB) Diesel Emission Control Strategy Verification Procedure ("Verification Procedure") pursuant to title 13, California Code of Regulations (CCR), sections 2700 to 2710. According to the Verification Procedure, a diesel emission control strategy (DECS) may not be verified unless a multimedia evaluation of the fuel has been conducted, pursuant to the California Health and Safety Code (H&SC) section 43830.8, and the California Environmental Policy Council (CEPC) has determined that there will not be a significant adverse impact on public health or the environment in comparison to diesel fuel meeting ARB motor vehicle diesel fuel specifications.

A. Multimedia Working Group

The California Environmental Protection Agency (Cal/EPA) formed the interagency Multimedia Working Group (MMWG) to oversee fuels multimedia evaluations. The MMWG includes representatives from the ARB, State Water Resources Control Board (SWRCB), Office of Environmental Health Hazard Assessment (OEHHA), and Department of Toxic Substances Control (DTSC). The members of the MMWG are listed in Appendix A. The MMWG consults with other sister agencies and other experts as needed (e.g., if there are potential pesticide impacts, staff from the Department of Pesticide Regulation can be consulted).

The multimedia evaluation of Viscon-treated diesel includes an assessment of potential impacts on air, water, and soil that may result from the production, use, and disposal of fuel treated with Viscon additive. In the evaluation, ARB staff was responsible for the air quality impact assessment and the overall coordination of the evaluation with the MMWG. SWRCB staff was responsible for the evaluation of surface water and groundwater quality and potential impacts. OEHHA staff was responsible for evaluating potential public health impacts. DTSC staff was responsible for evaluating potential hazardous waste and soil impacts.

B. Environmental Policy Council

Pursuant to the California Health and Safety Code (H&SC) section 43830.8, a multimedia evaluation must be conducted and peer-reviewed when ARB establishes a specification for a motor vehicle fuel. Before ARB establishes a motor vehicle fuel specification, the CEPC must determine if the proposed fuel specification poses a significant adverse impact on public health or the environment. In making its determination, the CEPC must consider the following:

- Emissions of air pollutants, including ozone-forming compounds, particulate matter, toxic air contaminants, and greenhouse gases.
- Contamination of surface water, groundwater, and soil.

- Disposal of waste materials, including agricultural residue, forest biomass, and municipal solid waste.

In addition to being required as part of a fuel specification rulemaking, a multimedia evaluation of fuel additives is a requirement set forth in the Verification Procedure. In order to be granted verification, a fuel additive that is undergoing the verification process must also undergo a multimedia evaluation conducted to the same exacting standards set forth in H&SC section 43830.8.

If the CEPC determines that a proposed fuel-additive verification poses a significant adverse impact on public health or the environment, or that alternatives exist that would be less adverse, the council is to recommend alternative measures that the ARB or other State agencies may take to reduce any adverse impact on public health or the environment.

C. <u>Viscon Fuel Additive</u>

Viscon is a diesel fuel additive that consists of one part ultra-high-molecular-weight (UHMW) polymer and 99 parts CARB diesel. The polymer component of Viscon is polyisobutylene (PIB), C_4H_8, a pure hydrocarbon polymer with a molecular weight of about 7 million Daltons. PIB is a food grade material that is non-toxic, colorless, tasteless, odorless and insoluble in water. PIB is commonly used in the production of adhesives, sealants, lubricants, coatings, and chewing gum.

The Viscon additive is used at a dose rate of approximately 500 parts per million (ppm) in diesel fuel. Therefore, the total amount of PIB in the treated fuel is approximately 5 ppm.

D. <u>Diesel Emission Control Strategy Verification</u>

The verification program is designed to support ARB's Diesel Risk Reduction Plan and various fleet rules. The fleet rules have various paths to compliance and may require fleets to retrofit existing engines with approved retrofit technologies. Generally, a diesel emission control strategy must achieve a minimum 25 percent reduction in particulate matter (PM) alone or PM and NOx in order to qualify for verification and be verified as a diesel emission control strategy under ARB's verification program. Therefore, in addition to being EPA-registered, a fuel additive must complete verification if emission reductions claims are made, and a multimedia evaluation is part of the verification process.

In accordance with the Verification Procedure, Viscon California, LLC submitted an application for the verification of their fuel additive. If the CEPC concurs with the recommendations by the MMWG and determines that Viscon additive does not pose any significant adverse impact on public health or the environment, Viscon additive will be verified for use with approved off-road applications only.

Based on the data provided in the verification application, and pursuant to the terms and conditions specified below, ARB staff finds that Viscon additive reduces emissions of diesel PM consistent with Level 1 strategies (greater than or equal to 25 percent reductions). The Executive Officer will determine if the fuel additive merits verification, and subject to specified terms and conditions, will classify Viscon additive as a Level 1 strategy, for the off-road applications listed in Table 1.

Table 1: Appropriate Applications for the Viscon™ Fuel Additive

Diesel Emission Control Strategy	Application
Viscon™ Fuel Additive	Off-road agricultural tractors, loaders, graders, excavators, port cranes, and other industrial equipment

Viscon California, LLC requested verification of Viscon additive for use with model year 1985 to 1995 unregulated, four-stroke, off-road diesel engines used in off-road equipment with horsepower (HP) ratings between 175 to 300 HP.

As stated in the Verification Procedure, DECS verified under the Executive Order must conform to all applicable California emissions regulations and any violation of the conditions specified in the verification Executive Order and the multimedia evaluation Resolution shall be grounds for withdrawal of the verification.

E. Multimedia Evaluation

As required under the verification procedure for fuel additives, Viscon California, LLC and the MMWG conducted a multimedia evaluation of Viscon pursuant to H&SC section 43830.8 and the *Guidance Document and Recommendations on the Types of Scientific Information Submitted by Applicants for California Fuels Environmental Multimedia Evaluations, June 2008* ("Multimedia Evaluation Guidance Document").

A multimedia evaluation consists of three tiers. Tier I is the preliminary review of the product, in which a search of existing literature on the fuel or fuel additive is made and knowledge gaps determined. Tier II is the risk assessment design or test protocol to fill the knowledge gaps identified during Tier I of the process. Tier III is the implementation of the Tier II test plan, resulting in a final report of the environmental effects of the fuel or fuel additive.

Before starting Tier III of the evaluation process, the MMWG identified the following knowledge gaps in the Viscon Tier I and Tier II reports:

- The fate and transport of Viscon-treated diesel in soil compared to CARB diesel in soil. This data gap included, but was not limited to, the biodegradability of Viscon-treated diesel in soil.

- The impacts of Viscon-treated diesel on soil cleanup.

Based on the proposed verification and information provided by Viscon California, LLC, the MMWG determined that once verified, the Viscon additive would have limited and controlled uses. The determination was based on the following information:

- The Viscon fuel additive is 1 part ultra-high-molecular-weight PIB and 99 parts CARB diesel.
- The Viscon fuel additive is used at a dose level in diesel of about 500 ppm, resulting in a PIB content of Viscon-treated diesel of about 5 ppm.
- Viscon will only be used for off-road equipment, including port cranes, generators, irrigation pumps, and drilling rigs; this represents about 150 to 200 locations.
- Currently, the Viscon additive is not being marketed within the State.
- After receiving verification:
    - The expected statewide consumption of Viscon additive will be about 10 gal/day, or 3,650 gal/year.
    - The expected statewide consumption of Viscon-treated diesel will be roughly 25,600 gal/day, or 9.3 million gallons per year (gal/year). Note that each year, approximately 4.5 billion gallons of diesel is sold statewide. Also, 9.34 million gal/year equates to approximately 0.2 percent of all diesel sold statewide.
- The Viscon additive is not currently stored in underground storage tanks (USTs), and Viscon California, LLC believes most Viscon-treated diesel will be stored above ground. While the Viscon additive is a heterogeneous liquid that will not separate when stored by itself, the MMWG did not evaluate Viscon-treated diesel for storage in USTs.

Although the MMWG found that the potential risks to public health and the environment from the use of Viscon were minimal, further testing and research were required in order to address the knowledge gaps identified by the MMWG. Viscon California, LLC contracted the University of Georgia (UGA) to conduct additional multimedia tests to address biodegradation and environmental fate and transport in soil, and based on the results of the tests, provide an analysis of potential impacts on soil cleanup methods.

The specific conditions and requirements are specified in two letters sent to Viscon California, LLC dated May 19, 2009, and November 24, 2009. The letters are provided in Appendix F.

1. Biodegradation and Environmental Fate and Transport Testing

The biodegradation and environmental fate and transport tests were conducted by UGA and were completed on January 4, 2011, by submittal of the final UGA report entitled, "Effect of Fuel Additive Viscon on the Environmental Fate of Diesel Fuel." The final report is provided in Appendix G.

Based on the biodegradation and environmental fate testing, UGA made the following overall conclusions:

- Addition of Viscon to diesel at 5 ppm concentration does not affect the biodegradation of Viscon-treated diesel.
- The Viscon additive would not have a practical effect on fuel migration in unsaturated field soils and would, therefore, be unlikely to affect remediation strategies used to mitigate the environmental impact of spills or leakage of Viscon-treated diesel fuels.

The report was first submitted on November 18, 2010. After reviewing the initial submittal of the report, the MMWG determined that the report was incomplete and unacceptable.

The key comments, questions, and concerns raised by the MMWG are provided in Appendix H and include the following:

- The report did not undergo scientific peer review prior to the MMWG.
- The test results did not fully support the conclusions made in the report. The analyses and technical explanations needed to be further developed to justify the conclusions made in the report.
- The rationale for, and conclusions from, the statistical analyses of the data were unclear. The MMWG requested a revised report that included an explanation of the statistical methods used and specific conditions and assumptions.
- The report did not address the potential impacts on soil cleanup when a spill occurs.
- In order to conduct an independent analysis of the results, the MMWG requested the raw data from the testing.

In response to the conclusions made in the report, the MMWG held internal meetings to discuss the group's comments and concerns. On December 13, 2010, the MMWG sent UGA and Viscon California, LLC comments on the report.

On December 14, 2010, the MMWG held a conference call with Viscon California, LLC and UGA to discuss and explain each of the comments. UGA did not agree with many of the comments by the MMWG. However, UGA revised the report and resubmitted it to the MMWG on January 4, 2011. After review of the revised report, the MMWG determined that the principal comments and questions were not addressed and that only minor edits were made.

To ensure that the MMWG had the analyses necessary to complete the review, the MMWG completed an independent analysis of the test data provided by UGA. Based on this analysis, the MMWG came to the following conclusions:

- There appears to be no difference in biodegradability in soils between the Viscon-treated diesel and untreated diesel.

- The flow rates of Viscon-treated diesel are approximately 30 percent slower than untreated diesel. The final report had indicated that there was no significant transport difference between the two fuels. However, based on the test results, slower migration of Viscon-treated diesel would allow more time for soil cleanup actions than untreated diesel before reaching the groundwater table. Therefore, the use of Viscon additive may provide positive impacts on soil cleanup methods.
- The test data and results confirmed the initial finding of the MMWG that the use of Viscon additive would not cause a significant adverse impact on public health or the environment.

The MMWG comments from both the November 18, 2010, and January 4, 2011, submittals are provided in Appendix H.

F. <u>External Scientific Peer Review</u>

Under H&SC section 43830.8(d), an external scientific peer review of the multimedia evaluation must be conducted in accordance to H&SC section 57004. The purpose of the peer review is to determine whether the scientific portions of the staff report are based upon "sound scientific knowledge, methods, and practices (H&SC section 57004(d)(2))."

The peer review process was initiated by submittal of a request memorandum to the manager of the Cal/EPA Scientific Peer Review Program. The memorandum was prepared by the ARB as the lead agency of the MMWG and included a summary of the nature and scope of the requested review, descriptions of the scientific issues to be addressed, and a list of recommended areas of expertise. Upon approval, the University of California, through an interagency agreement with Cal/EPA, identified five reviewers to complete the review. The memorandum is provided in Appendix I.

ARB sent the Staff Report and supporting documentation to each of the reviewers, including the Viscon Tier I, II, and III reports, test protocols, test results, and raw data.

The peer reviewers completed their individual reviews and submitted comments to the MMWG. The MMWG reviewed all of the peer review comments, addressed each of the comments in a written response and have, where appropriate, made revisions to the report. The MMWG held several internal meetings to discuss and address each of the comments from the reviewers.

In general, the peer reviewers determined that the conclusions and recommendations made by the MMWG were based upon sound scientific knowledge, methods, and practices, including the overall finding that Viscon, as conditioned in the multimedia evaluation, does not pose any significant adverse impact on public health or the environment.

The complete set of peer review comments are provided in Appendix J. Individual comments can generally be categorized as follows:

- Increased levels of 1,3 butadiene[1]
- Insufficient statistical information
- Characteristics of polyisobutylene
- Transport pathways including atmospheric, soil, and water
- Emissions testing and results including engine selection and pre- and post-durability data

The MMWG prepared responses and conducted independent analyses to address each of the comments received. The responses from the group and individual agencies are provided in Appendix K.

[1] OEHHA conducted a risk assessment for 1,3-butadiene in diesel exhaust. Evaluated at the highest level of increase, the attributed lifetime cancer risk calculated from the increase is 2.5×10^{-8}. Therefore, even with the highest reported increase of 1,3-butadiene, the estimated risk is less than one in a million. Please refer to the screening risk assessment by OEHHA on page 2 of Appendix K: MMWG Responses to Peer Review Comments.

II. Summary

This section provides the multimedia evaluation summaries prepared by ARB, SWRCB, OEHHA, and DTSC. The evaluations were based on the relative differences between diesel fuel meeting ARB motor vehicle fuel specifications and Viscon-treated diesel fuel. The potential environmental and public health impacts from changes to air emissions, water quality, soil cleanup, and hazardous waste generation were evaluated. The complete evaluations and supporting documentation are provided in the appendices.

A. Air Resources Board Evaluation

ARB staff completed an air quality assessment of Viscon-treated diesel fuel. The evaluation included a description of the emission testing protocol and emission impact analysis on criteria pollutants, toxic air contaminants, and ozone precursors. The complete evaluation report is provided in Appendix B.

1. Criteria Pollutants

The emissions test program included baseline testing and Viscon pre-durability and post-durability testing. Pre-durability testing occurred after the engine and the Viscon fuel additive completed a de-greening period of 25 to 125 hours. This time frame allows an engine to reach a semi-steady state condition in which the device can be actively incorporated into the system and ensure that emission reductions are the result of the DECS and not a cleansed engine. Post-durability testing occurred after the engine and fuel additive accrued an additional 1,000 hours of run time. This testing represents a portion of the engine's durable life. Post-durability testing allows for the reasonable assurance that the DECS is robust and will maintain the verified level of emission reductions over time.

The average of the pre- and post-durability test results were used to generate the net effect of the emission control strategy. An equal weight was given to each value before comparison to baseline results was made.

Baseline testing was conducted on a single engine using CARB ultra-low-sulfur diesel (ULSD) fuel and Viscon-treated ULSD fuel for both pre-durability and post-durability data. Viscon emissions test results were compared to baseline results for the overall impact resulting from the use of the additive.

Average particulate matter emissions decreased by 25 percent while oxides of nitrogen (NOx) increased by 2.9 percent.[2] Average emissions of nitric oxide (NO) increased by 2.5 percent, total hydrocarbons (THC) increased by 6.2 percent, carbon monoxide (CO) increased by 1.4 percent, and carbon dioxide (CO_2) decreased by 1.3 percent.

[2] ARB Verification Procedure, pursuant to title 13, CCR, section 2700 – 2710, requires a minimum 25% percent reduction in PM to qualify for the program. Section 2706(b)(1)(A) limits NOx increases to 10% above baseline.

2. Toxic Air Contaminants

ARB identified diesel PM as a toxic air contaminant in 1998, and determined that diesel PM accounts for about 70 percent of the toxic risk from all identified toxic air contaminants. Test results verify that the use of the Viscon additive reduces PM emissions by about 25 percent from off-road engines.

Other toxic emissions tests were conducted for various carbonyls, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs). Post-durability data generally yielded significantly lower emissions than pre-durability data. For the analysis of PAH emissions, only pre-durability tests were conducted. Pre- and post-durability tests were conducted for carbonyls and VOCs.

Overall toxics test results show significant decreases in most PAHs and carbonyls and moderate increases in some VOC emissions. One exception to the general emissions trends was 1,3-butadiene emissions, which were increased approximately 16-fold in post-durability testing. At the dosage rate and amount of additive used, the increase of toxic emissions, including 1,3-butadiene, would not significantly impact the levels in the ambient air.

3. Ozone Precursors

Test results show a slight increase in NOx emissions and some VOCs. THC emissions increased by 6.2 percent from baseline emissions levels. Post-durability emissions of NOx, THC, and various VOCs were generally lower than pre-durability emissions.

4. Greenhouse Gas Emissions

On average, pre- and post-durability test results show a 1.3 percent decrease of CO_2 from baseline. Pre-durability data show a 0.89 percent reduction, while post-durability data show a 1.6 percent reduction in CO_2 emissions.

B. State Water Resources Control Board Evaluation

State Water Board staff evaluated the data provided by Viscon California, LLC. This evaluation is specific to the different environmental impacts of Viscon-treated diesel and CARB diesel. Because of the limited scope of use identified in Viscon's verification application and proposed low concentrations of the Viscon additive, State Water Board staff do not regard PIB, for this purpose, an aquatic toxicity threat to either surface or groundwater. Therefore, Viscon-treated diesel is unlikely to pose a greater risk to the environment than that posed by CARB diesel alone. Please see Appendix C for the complete evaluation. State Water Board staff supports the ARB verification of Viscon-treated diesel.

C. Office of Environmental Health Hazard Assessment Evaluation

OEHHA staff assessed the public health impact from the use of Viscon as compared to diesel fuel based on the data provided by Viscon California, LLC. Please refer to Appendix D for the complete report.

In the overall evaluation of Viscon, OEHHA found that diesel engines burning Viscon-treated diesel fuel produce significantly less emissions of particles than do engines burning diesel fuel that meets current CARB specifications but do not contain the Viscon additive PIB. The additive component of Viscon fuel, high-molecular-weight PIB (HMWPIB), is a substance that is not volatile and is insoluble in water. When released in soil or on the surface of soil, it will remain at the point of release unless the soil is disturbed. It can be transported to aquatic sediment bound to re-suspended soil particles where it may be highly persistent. The toxicity of HMW PIB appears to be very low and uptake through skin or mucous membranes is expected to be very small due to the high molecular weight of the additive molecules. OEHHA finds that the use of Viscon-treated diesel fuel may reduce morbidity and mortality due to pulmonary diseases.

D. Department of Toxics Substances Control Evaluation

DTSC staff evaluated the potential impact of Viscon fuel on human health and the environment due to hazardous waste and constituent releases to the groundwater and soil. The evaluation of Viscon showed that the high molecular weight of PIB has very low toxicity and is inert in most chemicals. Other properties include insolubility in water, high viscosity, and low permeability. Please refer to Appendix E for staff's evaluation.

DTSC staff supports the ARB verification of Viscon based upon the air emission reductions achieved from the use of Viscon and low toxicity of the PIB additive. Viscon California, LLC completed the specified laboratory testing and analysis required by the MMWG to fill the knowledge gaps identified in the multimedia evaluation. While the initial report on this testing and analysis had shortcomings and the revised version failed to address all of the concerns identified by DTSC, DTSC staff have nevertheless concluded that the addition of Viscon additive does not appear to have a significant adverse impact on the biodegradability and transport of diesel in soil.

III. Conclusions

This section provides the conclusions of each of the evaluations conducted by ARB, SWRCB, OEHHA, and DTSC. The conclusions on the impacts of Viscon-treated diesel on public health and the environment are summarized below:

A. Conclusions on Air Emissions Impact

Based on a relative comparison between CARB diesel and Viscon, ARB staff concludes that the use of Viscon additive and the resulting air emissions do not pose a significant adverse impact on public health or the environment.

ARB staff also concludes the following about the use of the Viscon fuel additive:

- Viscon reduces emissions and health risk from PM in diesel exhaust, a toxic air contaminant identified by ARB.
- Emissions of certain toxic compounds may increase with the use of Viscon additive, but because of the conditions the ARB will impose on the use of the additive, such increases would not significantly impact ambient levels of those compounds.
- The air quality effects of the additive, either alone or in additized diesel fuel, are expected to be less than or equal to diesel fuel complying with ARB fuel regulations.

B. Conclusions on Water Impacts

SWRCB staff concludes that, given the relatively non-toxic nature of the additive polyisobutylene (PIB), its low dose rate of five ppm, and the insolubility of PIB in water, there are no more significant risks to beneficial uses of California waters posed by Viscon-treated diesel than that posed by CARB diesel alone. Additionally, the potential scope of any unanticipated impacts is limited given the limited and controlled use of Viscon additive in California diesel fuel, as described in the multimedia evaluation and ARB verification application.

C. Conclusions on Public Health Impact

OEHHA staff concludes that the use of Viscon-treated diesel fuel may reduce morbidity and mortality due to pulmonary diseases, including lung cancer in adults and allergic asthma in children, caused by substances in the particles contained in diesel exhaust.

D. Conclusions on Soil and Hazardous Waste Impact

DTSC staff supports the ARB verification of Viscon based upon the air emission reductions achieved from the use of Viscon and low toxicity of the PIB additive. Viscon California, LLC completed the specified laboratory testing and analysis required by the MMWG to fill the knowledge gaps identified in the multimedia evaluation.

IV. Recommendations

The Multimedia Working Group recommends that the CEPC:

1. Find that the limited and controlled use of Viscon additive in California diesel fuel, as described in the multimedia evaluation and verification application, does not pose a significant adverse impact on public health or the environment compared to untreated California diesel fuel.

2. Condition the finding on the following:

    a. Quarterly reports must be submitted to ARB for the first year after receiving verification and annual reports thereafter. The reports must provide the following information:
        i. California and national quarterly and annual sales of Viscon additive;
        ii. California and national quarterly and annual sales of total Viscon-treated diesel fuel; and
        iii. Identification of end users.

    b. In the event that the requested information, studies, or any other relevant available information indicate the potential for significant risks to the environment or public health, the use of Viscon additive will be reviewed by the CEPC for consideration of appropriate action.

    c. Require that combustion tests of Viscon-treated diesel fuel be performed in diesel engines with post-combustion oxidation devices before expanding the current verification or permitting the use of Viscon additive in on-road vehicles.

APPENDIX A

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APPENDIX B

Air Resources Board: Impacts Assessment of Viscon Diesel Fuel Additive on Exhaust Emissions from Heavy-Duty Diesel Engines

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State of California
California Air Resources Board

Impacts Assessment of Viscon Diesel Fuel Additive on Exhaust Emissions from Heavy-Duty Engines

January 21, 2011

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I. Summary, Conclusions, and Recommendations

A. Summary

The staff of the Air Resources Board (ARB) completed an air quality assessment of Viscon-treated diesel fuel. The evaluation assesses the impact Viscon diesel has on emissions from heavy-duty diesel engines. The relative comparison is between ultra-low-sulfur diesel (ULSD) fuel and Viscon-treated ULSD fuel. The evaluation includes an emission summary of criteria pollutants, toxic air contaminants, and ozone precursors.

Staff's assessment is based on the data submitted for the ARB Diesel Emission Control Strategy Verification and multimedia evaluation of Viscon, including the Viscon multimedia reports and test results from the emission studies conducted at Olson-Ecologic Engine Testing Laboratories (Olson Lab). The Viscon multimedia reports include background information on the fuel additive, test protocol, test results, and other supporting documentation.

1. Criteria Pollutants

The emissions test program includes ULSD baseline testing and Viscon diesel pre-durability and post-durability testing. Post-durability testing was conducted after completion of the thousand-hour durability test required for verification. One heavy-duty Caterpillar model 3306 engine was tested. Average pre- and post-durability results show that particulate matter (PM) emissions decreased by 25 percent while oxides of nitrogen (NOx) increased by 2.9 percent.

Carbon dioxide (CO_2) decreased by 1.3 percent, nitric oxide (NO) increased by 2.5 percent, total hydrocarbons (THC) increased by 6.2 percent, and carbon monoxide (CO) increased by 1.4 percent.

Based on the Viscon test results, post-durability tests yielded lower PM, NOx, THC, CO, and CO_2 emissions than pre-durability tests.

2. Toxic Emissions

Staff's evaluation of toxic emissions was based on the second set of testing conducted in 2006. Various unregulated emissions, including formaldehyde, benzene, and acetaldehyde were tested.

a. Particulate Matter Toxic Emissions

The ARB identified diesel PM as a toxic air contaminant (TAC) in 1998. Diesel PM has been determined to account for approximately 70 percent of the toxic risk from all identified TACs. Test results show a 25 percent reduction in diesel PM with the use of Viscon fuel additive.

b. Other Toxic Emissions

Emissions testing of polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and carbonyls were completed for the Viscon evaluation. PAH emissions were analyzed via gas chromatography and mass spectrometry by Desert Research Institute (DRI). Carbonyls were also analyzed by DRI via high performance liquid chromatography. VOCs were analyzed via gas chromatography by Olson Lab.

VOC and carbonyl emissions were tested pre-durability and post-durability. For PAH emissions, only pre-durability tests were conducted. Overall toxics test results show significant decreases in most PAHs and carbonyls and moderate increases in some VOC emissions.

At the dose rate and amount of additive used, the increase of certain toxic emissions would not significantly impact the levels in the ambient air.

3. Ozone Precursors

Ozone, a highly reactive compound composed of three oxygen atoms, is a primary component of smog and is recognized and regulated as a serious air pollutant. Ozone can damage the lungs and airways. It inflames and irritates respiratory tissue and can worsen symptoms of asthmatic people. It causes symptoms such as coughing, chest tightness, and impaired breathing. Elevated exposures can cause permanent lung damage, while repeated exposure can increase the risk of premature death in persons with poor health. NOx, THC, and VOCs are ozone precursors.

Average Viscon test results show a 2.9 percent increase in NOx compared to baseline emissions, and a 6.2 percent increase in THC emissions.

Viscon test data confirm that post-durability emissions of most toxics were lower than pre-durability emissions. THC pre-durability results show a 9.1 percent increase from baseline but post-durability results show a 3.8 percent increase. Similar trends were found for NOx and various VOC emissions.

4. Greenhouse Gas Emissions

Greenhouse gases, such as carbon dioxide (CO_2), trap heat in the atmosphere and are emitted through natural processes and human activities. Average CO_2 emissions were reduced by 1.3 percent from baseline emissions. Pre-durability data show a 0.89 percent reduction, while post-durability data show a 1.6 percent reduction in CO_2 emissions.

B. Conclusions

Based on a relative comparison between ULSD fuel and Viscon-treated diesel fuel, ARB staff concludes that the use of Viscon additive does not pose a significant adverse impact on public health or the environment from potential air quality impacts.

ARB staff also concludes the following about the use of the Viscon fuel additive:

- Viscon reduces emissions and health risk from PM in diesel exhaust, a toxic air contaminant identified by ARB.
- Emissions of certain toxic compounds may increase with the use of Viscon additive, but because of the conditions the ARB will impose on the use of the additive, such increases would not significantly impact ambient levels of those compounds.
- The air quality effects of the additive, either alone or in additized diesel fuel, are expected to be less than or equal to diesel fuel complying with ARB fuel regulations.

C. Recommendations

Based on the air quality assessment and evaluation of emission impacts from the use of Viscon, ARB staff recommends that the Environmental Policy Council find that the use of Viscon additive, as described in the Viscon multimedia evaluation, does not pose a significant adverse impact on human health or the environment from potential air quality impacts, relative to conventional California diesel fuel.

II. Introduction

Viscon California, LLC (Viscon California) designed its diesel fuel additive, Viscon, to reduce PM and other harmful emissions from diesel-fueled engines.

Viscon California requested that the ARB verify their fuel additive, Viscon, as a diesel emission control strategy pursuant to title 13, California Code of Regulations (CCR), sections 2700 - 2710. According to the verification procedure, Viscon may not be verified unless a multimedia evaluation of the additive has been conducted and the California Environmental Policy Council (CEPC) determines that there will not be a significant adverse impact on public health or the environment in comparison to diesel fuel meeting the ARB motor vehicle diesel fuel specifications.

The multimedia working group (MMWG), with representatives from the ARB, the State Water Resources Control Board (SWRCB), the Office of Environmental Health Hazard Assessment (OEHHA), and the Department of Toxic Substances Control (DTSC), conducted a multimedia evaluation. The multimedia evaluation includes the impact on air, water, and soil that may result from the production, use, and disposal of Viscon.

For the multimedia evaluation of Viscon, ARB staff was responsible for the air quality impact assessment and the overall coordination of the multimedia evaluation and the MMWG. SWRCB staff was responsible for the evaluation of surface and groundwater quality and potential impacts. OEHHA staff was responsible for evaluating potential human health impacts. DTSC staff was responsible for evaluating potential hazardous waste and soil impacts.

Pursuant to the California Health and Safety Code (H&SC) section 43830.8, a multimedia evaluation must be conducted and peer-reviewed when ARB establishes a specification for a motor vehicle fuel. Before adoption of a new or modified motor vehicle fuel specification, the CEPC must determine if the proposed fuel specification poses a significant adverse impact on public health or the environment. The multimedia evaluation of Viscon is not a proposed rule, but a requirement set forth in the ARB verification procedure. In order to be granted verification, a multimedia evaluation must be conducted with respect to the same exacting standard as the requirements set forth in H&SC section 43830.8.

III. Description and Potential Use of Viscon Fuel

Viscon is a diesel fuel additive consisting of one part ultra-high-molecular-weight polyisobutylene (PIB) polymer and 99 parts diesel. The Viscon additive would be used at a dose rate of approximately 500 parts per million (ppm) in diesel fuel. Therefore, the PIB content in Viscon-treated diesel is about 5 ppm.

Ultra-high-molecular PIB is a food grade material that is non-toxic, colorless, tasteless, odorless, and insoluble in water. PIB is commonly used in the production of adhesives, sealants, lubricants, coatings, and chewing gum.

Viscon is being verified for use in off-road equipment, including port cranes, generators, and irrigation pumps. Under the proposed verification, the Viscon additive will be verified for use with unregulated 1985 through 1995 off-road diesel engines manufactured by Caterpillar Inc. and Cummins Inc. After receiving verification, the expected statewide consumption of Viscon is reported to be approximately ten gallons per day, or 3,650 gallons per year.

IV. Exhaust Emissions

Engine emissions testing was performed to characterize regulated emissions, including PM, NOx, CO, and THC, and various unregulated toxic emissions. Viscon California contracted Olson Lab to conduct comparative emissions tests to determine the emission impacts of Viscon-treated diesel fuel and the baseline CARB diesel fuel.

A. Engine Emission Testing

Emission testing was conducted in 2003 and also in 2006. The 2006 test results and exhaust emissions data were used for the Viscon multimedia evaluation and verification. Since the 2003 results did not support the verification because of the test fuel change and the use of the single filter method, these results were not included in staff's evaluation of multimedia effects and air quality impacts.

In 2006, Viscon California conducted a second set of emission tests, pursuant to the verification procedure. The following is a summary of the testing parameters:

- Test Cycle: ISO 8178 C1, 8-Mode Off-Road Emissions Test Cycle
- Reference Fuel: No. 2 ultra-low-sulfur diesel (ULSD)
- Candidate Fuel: Viscon diesel (ULSD additized with Viscon additive)
- Test Engine: Caterpillar 3306 diesel engine
- Emissions characterized: Criteria and Toxic Air Pollutants

1. Test Engine and Test Fuel

All emissions and durability tests were conducted on a 1986 Caterpillar 3306 engine. The test engine used in the test program was an unregulated six-cylinder, 265 horsepower, 1986 model year, Caterpillar 3306 heavy-duty diesel engine. The same test engine was used for both 2003 and 2006 tests.

The verification procedure requires at least one engine be tested to represent the emission control group. Durability testing requirements state that the engine and application used in the durability demonstration must be representative of the emission control group for which verification is sought.

As required of each verification applicant, it is the responsibility of Viscon California to define emission control groups that are appropriate for the diesel emission control strategy (DECS). An emission control group is defined as a set of diesel engines and applications determined by parameters that affect the performance of a particular strategy. Viscon California requested to verify Viscon additive for use with unregulated 1985 through 1995 off-road diesel engines manufactured by Caterpillar Inc. and Cummins Inc. Based on the technical analysis provided in the verification application, staff accepts and recommends verification of the requested emission control group.

The test fuel used in the 2006 testing program was No. 2 ultra-low-sulfur diesel (ULSD) fuel. The complete test program was conducted on one batch of commercially available

No. 2 ULSD fuel. Previous testing was conducted using No. 2 low-sulfur diesel fuel (LSD).

2. Test Cycle

Emission testing was conducted on an engine dynamometer using the ISO 8178 C1, 8-mode test cycle. ISO 8178 is a collection of many steady-state test cycles, each representing a sequence of steady-state modes with different weighting factors. The specific engine modes and their weighting factors are listed in Table 1.

Table 1. ISO 8178 C1 8-Mode Test Cycle

Mode Number	Weighting Factor, %	RPM	Torque, %
1	15	Rated	100
2	15	Rated	75
3	15	Rated	50
4	10	Rated	10
5	10	Max torque, RPM	100
6	10	Max torque	75
7	10	Max torque	50
8	15	Idle	0

Emissions were recorded every second of each mode for five minutes to stabilize emissions. The last two minutes of each mode were recorded to provide the stabilized, second-by-second, steady-state emissions results.

All engine exhaust passed through the Horiba dilution tunnel. The dilution tunnel was operated to provide variable exhaust dilution for each mode as a function of actual exhaust flow rates. The measured dilution ratios were expected to be relatively constant for the same mode for all tests, but the actual dilution ratios were used as a measure of individual tests to allow for test-to-test variance.

Particulate sampling required initial calculation of exhaust mass flow rate per mode from an actual full 8-mode test. Secondary dilution ratios were programmed for each mode and time of sampling were adjusted to compensate for the appropriate model weighting factors. Since the PM sampler draws samples from the exhaust dilution tunnel for each mode, the dilution ratio was included in the calculation of the generated particulates in grams per brake horsepower hour (g/bhp-hr).

Toxics tests were then completed via exhaust sampling and gas chromatography (GC). Modal sample collection was done for a total of 20 minutes. Samples were drawn from each bag and analyzed. The overall dilution ratio from the 8-modes was used to correct and calculate the resulting GC data in g/bhp-hr. Samples were simultaneously drawn and captured for PAH and carbonyl analyses at DRI.

3. Pre-durability and Post-durability

Pre-durability and post-durability tests were conducted under the same conditions and test methods as baseline testing. Pre-durability testing occurred after the engine and the Viscon fuel additive completed a de-greening period of 25 to 125 hours. This time frame allows an engine to reach a semi-steady state condition in which the device can be actively incorporated into the system and ensure that emission reductions are the result of the DECS and not a cleansed engine.

Post-durability testing occurred after the engine and fuel additive accrued an additional 1,000 hours of run time. This testing represents a portion of the engine's durable life. Post-durability testing allows for the reasonable assurance that the DECS is robust and will maintain the verified level of emission reductions over time.

The average of the pre- and post-durability test results were used to generate the net effect of the emission control strategy. An equal weight was given to each value before comparison to baseline results were made.

B. Results

Brake-specific emissions for regulated emissions, including PM, NOx, CO, THC, and selected unregulated toxic emissions were obtained from the testing.

1. Viscon Criteria Pollutant Emissions Results

Emissions data and testing results were reported for both 2003 and 2006 tests. In support of the verification of Viscon, only the 2006 test data were used in the air quality assessment and multimedia evaluation of Viscon.

Emissions results were reported for both pre-durability and post-durability Viscon diesel tests. Baseline and pre-durability tests were completed in 2007. Post-durability tests were completed in 2008. A total of nine official tests were run on the baseline fuel. Viscon diesel testing included nine official pre-durability tests and eleven post-durability tests. The average results, percent change compared to baseline, and standard deviation of the results are presented in the summary tables provided.

Average pre-durability and post-durability results show a 25 percent reduction in PM and a slight increase in NOx. Although results show a 2.9 percent increase in NOx, the increase is not statistically significant due to the variability of the baseline data. For the baseline results, the standard deviation was 0.213, while pre- and post-durability standard deviations were 0.166 and 0.142, respectively.

Listed in Table 2 are the baseline and Viscon pre- and post-durability test results including the standard deviation of each set of results.

Table 2. Summary of Criteria Pollutant Emission Results[1]

Pollutant	Baseline ULSD		Viscon Pre-Durability			Viscon Post-Durability			Avg Pre and Post	
	Average g/bhp-hr	Standard Deviation	Average g/bhp-hr	Standard Deviation	Percent Change	Average g/bhp-hr	Standard Deviation	Percent Change	Average g/bhp-hr	Percent Change
PM	0.265	0.0236	0.202	0.0211	-24%	0.197	0.00571	-25.7%	0.199	-25%
THC	1.38	0.0330	1.50	0.0296	9.1%	1.43	0.0360	3.84%	1.46	6.2%
CO	1.69	0.0287	1.83	0.0406	7.9%	1.63	0.0672	-3.90%	1.72	1.4%
NO	5.14	0.156	5.08	0.0902	-1.2%	5.43	0.122	5.55%	5.27	2.5%
NOx	5.79	0.213	6.04	0.166	4.2%	5.90	0.142	1.87%	5.96	2.9%
CO2	561	1.89	556	2.29	-0.9%	552	2.92	-1.62%	554	-1.3%

[1]Average values calculated from test results provided in Table 1, Viscon Tier II Multimedia Report, Tab 8

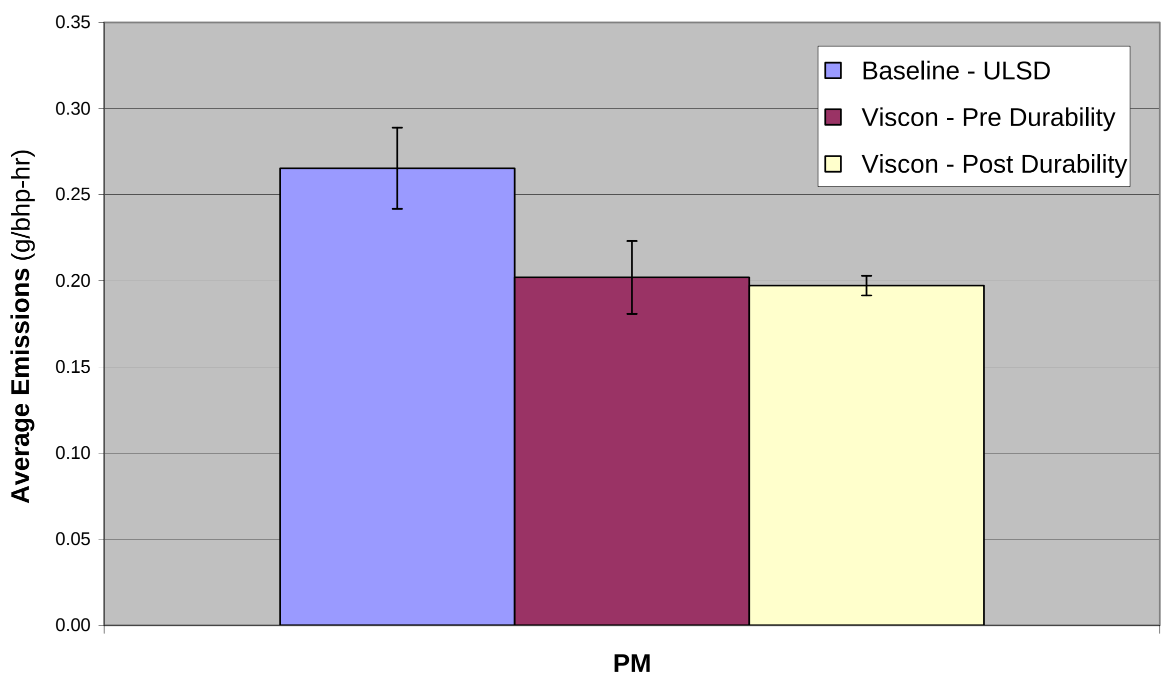
As listed, THC increased by an average 6.2 percent, CO increased by 1.4 percent, and CO_2 decreased by 1.3 percent from baseline.

2. Viscon Toxic PM Emissions Results

On average, pre- and post-durability results show a 25 percent reduction in PM. As summarized in Table 2, post-durability test results show greater reductions in PM emissions than pre-durability test results.

Figure 1 illustrates the average PM results from baseline and Viscon testing, including pre-, post-, and average pre- and post-durability. The graph depicts the reduction in PM over baseline emissions. The error bars illustrate the standard deviation of each set of results.

Figure 1. Comparison of Baseline and Viscon PM Emission Results



3. Other Viscon Toxic Emissions Results

Toxics testing was conducted for various polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and carbonyls. Samples were drawn and captured at Olson Laboratories. Toxics analyses were conducted by DRI staff. Pre-and post-durability toxics data were collected for VOCs and carbonyls. Pre-durability data were collected for PAHs. Triplicate sets of data were obtained for both the baseline reference fuel and the candidate Viscon-treated fuel.

Compared to baseline, toxics data show significant decreases of most PAHs and carbonyls, and moderate increases in some VOCs.

Average pre-durability results show that all PAH emissions decreased except for dibenzo(ah+ac)anthracene and benzo(ghi)perylene. Dibenzo(ah+ac)anthracene increased by approximately 250% from baseline, an approximate 0.17 ng/bhp-hr increase. For benzo(ghi)perylene, average baseline results were below the detection limit. All other PAH emissions were reduced by 16 to 100 percent compared to baseline emissions.

Table 3 is the summary of the PAH results, including the calculated standard deviation of each set of data, and calculated percent change from baseline.

Table 3. Summary of PAH Results[1] (µg/bhp-hr)

PAH	Baseline ULSD		Viscon Pre-Durability		
	Average µg/bhp-hr	Standard Deviation	Average µg/bhp-hr	Standard Deviation	Percent Change
naphthalene	10.5	2.98	4.61	0.588	-56%
2-methylnaphthalene	9.76	1.42	2.58	1.14	-74%
phenanthrene	1.34	0.0410	0.503	0.830	-63%
acenaphthene	0.659	0.0751	0.0644	0.156	-90%
fluorene	0.535	0.0221	0.131	1.27	-76%
acenaphthylene	0.193	0.0117	0.162	1.19	-16%
pyrene	0.227	0.0147	0.126	0.0428	-45%
anthracene	0.181	0.0102	0.0748	0.268	-59%
flouranthene	0.0673	0.00811	0.0503	0.250	-25%
chrysene-triphenylene	0.0118	0.00200	0.00533	0.00540	-55%
benz(a)anthracene	0.0076	0.000721	0.00153	0.0417	-80%
benzo(b+j)flouranthene	0.000933	0.000577	0.000333	0.0425	-64%
BeP	0.000833	0.000404	0.000533	0.00690	-36%
BaP	0.000400	0.000529	0.000000	0.0239	-100%
benzo(k)flouranthene	0.000333	0.000153	0.000167	0.0238	-50%
perylene	0.000267	0.000306	0.00000000	0.00564	-100%
indeno[123-cd]pyrene	0.000133	0.000231	0.0000667	0.00168	-50%
dibenzo(ah+ac)anthracene	0.0000667	0.000115	0.000233	0.0215	250%
benzo(ghi)perylene	ND[2]	ND[2]	0.000133	0.0304	NC[3]

[1]Average values calculated from test results provided in the Viscon Tier II Multimedia Report, Tab 8
[2] ND – Not Detected; Below detection limit
[3] NC – Not Calculated; Percent change not calculated because the reported baseline emission rate was 0

Most VOCs increased with the use of Viscon. Only pre-durability test results show reductions in some VOCs, including orthro-, meta-, and para-xylene. Average pre- and post-durability results show moderate to high increases of some VOCs, including 1,3-butadiene, benzene, toluene, and ethylbenzene.

On average, benzene and toluene increased by 23 and 31 percent, respectively. Differing between pre- and post-durability, post-durability results show a 2.3 percent increase of benzene, compared to 43 percent increase pre-durability.

1,3-butadiene had the highest reported increase from baseline. On average, 1,3-butadiene increased by approximately 770% from baseline (4.14 mg/bhp-hr increase). As reported in Table 4, pre-durability 1,3-butadiene data were below the detection limit, but post-durability data show an increase of about 1,640% from baseline. Toxics tests for 1,3-butadiene is highly sensitive as the product can degrade differently under varying conditions. In order to further assess the risk involved with such drastic post-durability increases, OEHHA conducted an additional risk assessment for 1,3-butadiene in diesel exhaust. Evaluated at the highest level of increase, the attributable lifetime cancer risk calculated from the increase is 2.5×10^{-8}. Therefore, even with the highest reported increase of 1,3-butadiene, the estimated risk is less than 1 in a million. The complete results of this analysis may be found in the peer review section of the staff report from OEHHA.

Table 4 provides the pre-, post-, and average pre- and post-durability VOC emission results, standard deviations, and percent changes compared to baseline emissions.

Viscon diesel increased some carbonyls, including formaldehyde and acetaldehyde, and decreased other carbonyls, such as methyl ethyl ketone, acetone, and valeraldehyde. Pre-durability test results show a general increase in carbonyls but post-durability results showed a general decrease. Formaldehyde results show a significant decrease in emissions, from 23 to 10 percent increase from pre- to post-durability data. Acetaldehyde decreased by 6 percent; however, initial results show an increase from baseline emissions. The results determine that post-durability toxic emissions were generally less than pre-durability emissions.

Table 5 provides carbonyl results from the testing, including the calculated standard deviation of each set of triplicate data collected and the percent change from baseline emissions.

Table 4. Summary of VOC Results[1] (mg/bhp-hr)

VOC	Baseline ULSD		Viscon Pre-Durability			Viscon Post-Durability			Average Pre and Post	
	Average mg/bhp-hr	Standard Deviation	Average mg/bhp-hr	Standard Deviation	Percent Change	Average mg/bhp-hr	Standard Deviation	Percent Change	Average mg/bhp-hr	Percent Change
1,3-butadiene	0.252	0.0000445	ND[1]	--	--	4.39	0.0006321	1640%	2.20	770%
benzene	9.03	0.000468	12.9	0.001040	43%	9.24	0.000560	2%	11.1	23%
toluene	4.23	0.000249	6.04	0.000180	43%	5.02	0.000103	19%	5.53	31%
ethylbenzene	1.81	0.000211	2.11	0.000079	16%	2.46	0.000059	36%	2.29	26%
m&p-xylene	3.90	0.000146	2.91	0.000158	-25%	4.00	0.000146	3%	3.46	-11%
o-xylene	2.31	0.000308	1.80	0.000032	-22%	2.57	0.000308	11%	2.18	-5%

[1]Average values calculated from test results provided in the Viscon Tier II Multimedia Report, Tab 8
[2] ND – Not Detected; Below detection limit
[3] NC – Not Calculated; Percent change not calculated because the emission rate for 1,3-butadiene was below the detection limit.

Table 5. Summary of Carbonyl Results[1] (mg/bhp-hr)

Carbonyls	Baseline ULSD		Viscon Pre-Durability			Viscon Post-Durability			Average Pre and Post	
	Average mg/bhp-hr	Standard Deviation	Average mg/bhp-hr	Standard Deviation	Percent Change	Average mg/bhp-hr	Standard Deviation	Percent Change	Average mg/bhp-hr	Percent Change
formaldehyde	27.3	0.000564	33.5	0.00212	23%	30.0	0.00344	10%	31.7	16%
acetaldehyde	7.39	0.000163	9.28	0.000460	26%	6.95	0.000612	-6%	8.11	10%
butyraldehyde	4.76	0.000342	4.03	0.000120	-15%	0.558	0.0000752	-88%	2.29	-52%
acetone	1.87	0.000137	2.64	0.000222	41%	0.885	0.000684	-53%	1.76	-6%
propionaldehyde	1.33	0.000024	1.51	0.000120	14%	1.09	0.0000544	-18%	1.30	-2%
acrolein	1.03	0.000330	1.82	0.000330	77%	0.672	0.000595	-34%	1.25	21%
crotonaldehyde	1.00	0.0000822	1.19	0.000070	19%	0.332	0.000490	-67%	0.759	-24%
benzaldehyde	0.633	0.0000176	0.724	0.000286	14%	0.489	0.000227	-23%	0.607	-4%
valeraldehyde	0.617	0.000135	0.496	0.000085	-20%	0.000	0.000000	-100%	0.248	-60%
methyl ethyl ketone	0.462	0.0000597	0.480	0.0000407	4%	0.105	0.000118	-77%	0.293	-37%
methacrolein	0.447	0.0000615	0.562	0.0000681	26%	0.036	0.0000329	-92%	0.299	-33%
glyoxal	0.322	0.000164	0.669	0.0000544	107%	0.000	0.000000	-100%	0.334	4%
hexanaldehyde	0.316	0.0000304	0.368	0.0000923	17%	0.395	0.0000696	25%	0.382	21%
m-tolualdehyde	0.0163	0.00000751	0.109	0.0000144	569%	0.223	0.000102	1263%	0.166	916%

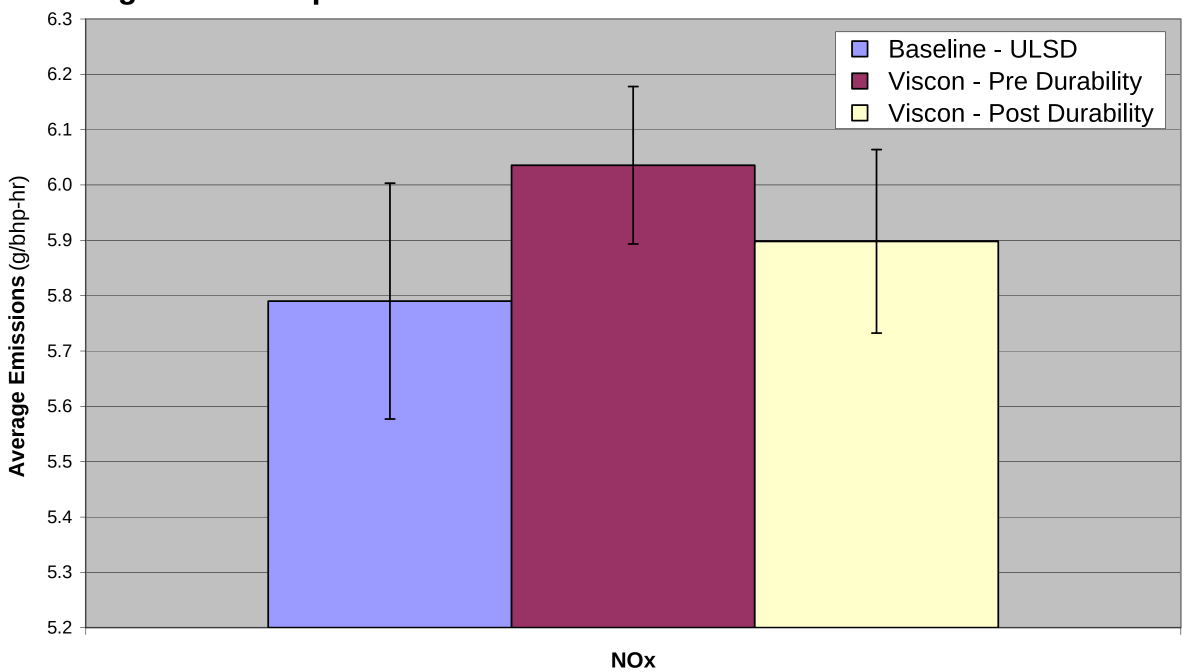
[1]Average values calculated from test results provided in the Viscon Tier II Multimedia Report, Tab 8

4. Ozone Precursors

Average test results show a 2.9 percent NOx increase compared to baseline. A total increase of about 0.17 g/bhp-hr NOx was reported with high standard deviations of 0.213, 0.166, 0.142 for baseline, pre-durability, and post-durability tests, respectively.

Figure 2 is a graphical summary of the results from the baseline and Viscon pre- and post-durability tests. As shown in the figure, the standard deviation of each set of tests is illustrated by the error bars on the graph. The error bars show the wide variability and spread between tests.

Figure 2. Comparison of Baseline and Viscon NOx Emission Results



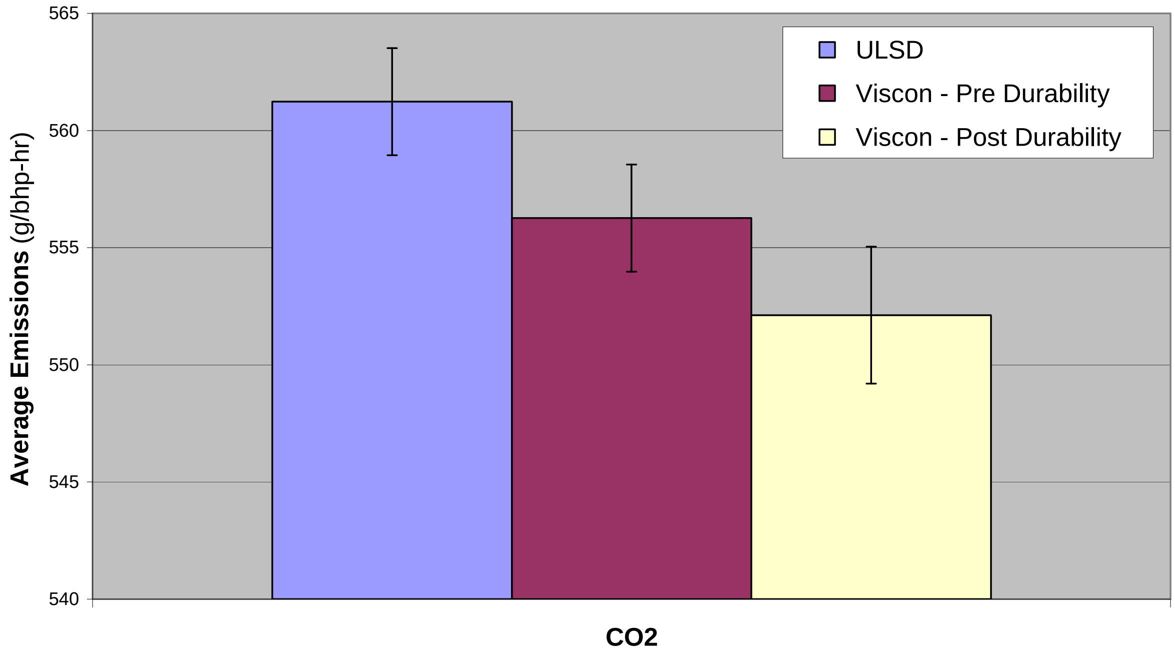
Average THC emissions increased by 6.2 percent from baseline emissions levels. Some VOC emissions also increased. At the limited dose rate of Viscon, the increase in emissions of these toxics would not significantly impact emission levels in the ambient air. Post-durability emissions of NOx, THC, and various VOCs, were generally lower than pre-durability emissions.

5. Greenhouse Gas Emissions

Average pre-and post-durability tests show a CO_2 reduction of about 1.3 percent with the use of Viscon. Pre-durability data show a CO_2 reduction of about 0.89 percent while post-durability data show an increased CO_2 reduction of about 1.6 percent.

Figure 3 illustrates the CO_2 test results compared to baseline results.

Figure 3. Comparison of Baseline and Viscon CO_2 Emission Results



V. References

[1] Las Palmas Oil and Dehydration Company, Viscon Multi Media Evaluation (Tier I), Final Report prepared for the California Air Resources Board. October 24, 2008.

[2] Las Palmas Oil and Dehydration Company, Viscon Multi Media Evaluation (Tier II), Final Report prepared for the California Air Resources Board. March 16, 2009.

[3] Viscon California, LLC. Viscon Multi Media Evaluation (Tier III) Summary, Final Report prepared for the California Air Resources Board. June 3, 2009.

[4] Olson-EcoLogic Engine Testing Laboratories, Engine and Fuel Testing to Measure Exhaust Emissions from a Model 3306 Caterpillar Diesel Engine, Final Report prepared for Viscon California. December 1, 2006.

[5] Olson-EcoLogic Engine Testing Laboratories, Proposal and Test Plan to Conduct 1000 Hours Durability and Subsequent Emission Testing with Viscon Treated Ultra Low Sulfur Diesel Fuel While Operating a Model 3306 Caterpillar Heavy-Duty Diesel Engine, Final Report prepared for Viscon California. November 13, 2006.

[6] Letter of Conditional Approval, May 19, 2009.

[7] Letter of Conditional Approval, Amended, November 24, 2009.

APPENDIX C

State Water Resources Control Board: Viscon Evaluation

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Viscon Evaluation

Water Board Staff Evaluation – Background

Viscon-treated diesel is a blend of 99.9995% CARB diesel with 0.0005% polyisobutylene (PIB).

State Water Board staff evaluated data provided by Viscon California, LLC on the impacts to surface and groundwater quality due to various release scenarios of diesel treated with Viscon-treated diesel. State Water Board staff evaluation is specific to any differential environmental impacts between Viscon-treated diesel and CARB diesel.

Staff conclusions identified below are limited in scope as Viscon California, LLC verification application to CARB only included off-road use and indicated Viscon-treated diesel would not be stored in underground storage tanks (USTs).

The following elements were considered by State Water Board staff in its evaluation of Viscon-treated diesel.

Material Compatibility

According to the Tier I document, Viscon-treated diesel will be used exclusively in a limited number of off-road applications (e.g. generators at construction sites) and that none of those sites will include storage in USTs. Therefore material compatibility was not studied.

Biodegradability and Fate/Transport

Viscon California, LLC did not provide data on the biodegradability or fate and transport of Viscon-treated diesel but did submit material property data on the additive ingredient PIB. The Tier I report indicates that PIB is "completely insoluble in water" and may have a molecular weight as high as 4,000,000. Both factors suggest that PIB is not likely to travel far in soil or groundwater or enhance the ability of diesel to travel further in soil or groundwater.

These properties also suggest that PIB may not be very biodegradable, and thus PIB may accumulate in the soil in the immediate area of a surface spill. While the accumulation of an almost inert high molecular weight polymer in soil could theoretically fill voids sufficiently to inhibit the rate of infiltration from a surface spill, such accumulation in the soil may also affect the soil cleanup. However, this accumulation is unlikely due to the proposed very low concentration of the Viscon additive in diesel.

Aquatic Toxicity

Viscon California, LLC did not provide aquatic toxicity data on Viscon-treated diesel, but rather data on the toxicity of PIB itself.

According to the data provided in the Tier I, PIB is FDA approved for food applications in amounts more than a 1000 times greater than the proposed use of the Viscon additive. According to Tier I PIB is “completely insoluble in water”, and “virtually odor-free and tasteless”. Because of the limited scope of use identified in Viscon’s verification application and proposed low concentrations of the Viscon additive, State Water Board staff do not regard PIB, for this purpose, an aquatic toxicity threat to either surface or groundwater. Likewise, Viscon-treated diesel is unlikely to pose a greater risk to the environment than that posed by CARB diesel alone.

PIB has multiple FDA approved applications related to contact with, or components of, food products including linings or interior coatings of food containers and as an ingredient in chewing gum. Due to the relatively non-toxic nature of PIB, State Water Board staff does not believe additional aquatic toxicity testing needs to be done at this point, especially given the limited applications of Viscon additive and Viscon-treated diesel.

Wastewater Discharge from Manufacturing

Viscon additive is produced in Bakersfield, California, simply by mixing PIB into diesel. No water is used in the process and no wastewater is created.

Conclusions Regarding Viscon Water Impacts

State Water Board staff concludes that, given the relatively non-toxic nature of the additive PIB, its low dose rate of 5 ppm, and the insolubility of PIB in water, there are no more significant risks to beneficial uses of California waters posed by Viscon-treated diesel than that posed by CARB diesel alone. The potential scope of any unanticipated impacts is limited given the limited and controlled use of Viscon-treated diesel as described in the multimedia evaluation and CARB verification application.

APPENDIX D

Office of Environmental Health Hazard Assessment: Staff Report on Health Impacts of Viscon Diesel Fuel

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Staff Report on Health Impacts of Viscon Diesel Fuel

January 2010

Integrated Risk Assessment Branch and
Air Toxics and Epidemiology Branch
Office of Environmental Health Hazard Assessment
California Environmental Protection Agency

Overall evaluation and recommendations

Diesel engines burning Viscon diesel fuel produce significantly less emissions of particles than do engines burning diesel fuel that meets current CARB specifications but does not contain the Viscon additive polyisobutene. OEHHA scientists conclude that use of Viscon diesel fuel may reduce morbidity and mortality due to pulmonary diseases, including lung cancer in adults and allergic asthma in children, caused by substances in the particles contained in diesel exhaust. Information on human health impacts of diesel exhaust can be found in the June, 1998 Staff Report of the ARB and OEHHA, "Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant."

The additive component of Viscon fuel, high-molecular-weight polyisobutene (HMWOIB), is a substance that is not volatile and is insoluble in water. When released in soil or on the surface of soil, it will remain at the point of release unless the soil is disturbed. It can be transported to aquatic sediment bound to resuspended soil particles where it may be highly persistent. The toxicity of HMWPIB appears to be low and uptake through skin or mucous membranes is expected to be very small due to the high molecular weight of the additive molecules.

Diesel engines burning Viscon fuel emit larger amounts of certain aldehydes and unsaturated hydrocarbons than do engines burning ultra low sulfur diesel (ULSD) fuel. Because the absolute amount of these substances in diesel exhaust is small, there does not appear to be a significant increase in the risk of cancer from any of the increases in emissions. The increase in ambient levels of formaldehyde and acetaldehyde is estimated to be less than 0.01%. Increased emissions of aldehydes may, however, result in a small increase in irritation of mucous membranes of the respiratory system. Because it is plausible that a larger increase may increase the risk of severe asthma episodes, OEHHA recommends that combustion tests of Viscon be performed in diesel engines with post-combustion oxidation devices before permitting use of Viscon in on-road diesel vehicles.

Introduction

Viscon blended fuel is a diesel fuel made by combining an additive, polyisobutene, to diesel fuel that meets current California Air Resources Board (CARB) fuel specification regulations for motor vehicle diesel fuel (CARB diesel). The additive is synthesized by polymerizing isobutene into a high-molecular-weight organic molecules with repeating —$CH_2C(CH_3)_2$— moieties. The polyisobutene molecules in the additive vary in molecular weight around a value of approximately 10^7 Daltons and is termed high-molecular-weight polyisobutene (HMWPIB). When the additive is blended with CARB diesel, the concentration of HMWPIB is approximately 5 ppm.

HMWPIB has been used in consumer products including cosmetics and chewing gum. As a food additive, it has been evaluated by the United States

Food and Drug Agency (USFDA) and classified as ‘generally regarded as safe” (GRAS). However, no studies of mammalian toxicity or environmental toxicity of HMWPIB were provided to OEHHA by the applicant.

Toxic effects of polyisobutene.

OEHHA staff identified reports of toxicity tests of polyisobutene (PIB). Most of the reports contain results from toxicity testing of low-molecular-weight polyisobutene (LMWPIB), and these are summarized in this section along with several toxicituy tests of HMWPIB.

The acute toxicity of LMWPIB is low. Davis (1976) treated mice with a single oral dose of 89.6 g/kg and reported no deaths. As reviewed by the Cosmetic Ingredient Expert Review Panel (2007), LMWPIB applied to skin or eyes of laboratory animals produced irritation in a minority of animals tested, and this reaction when present was described as slight. LMWPIB did not appear to sensitize skin of Guinea pigs but was associated with contact dermatitis due to delayed hypersensitivity in a clinical case report (Parslew, 1996). LMWPIB implanted into the mandible of Guinea pigs did not cause inflammation or other reactions.

Studies of mutagenic and genoclastic effects of PIB were not found in results of literature searches. One study of the potential for PIB to transform mammalian cells was found. LMWPIB did not transform Syrian hamster embryo (SHE) cells, but it was positive as a promoter in a two-stage initiation-promotion transformation assay using NIH C3H 10T1/2 C18 cells (Aarsaether *et al*., 1987). No effects on survival, gross anatomy or microscopic anatomy were found in a 3-generation reproductive study of Charles River rats given 20,000 ppm LMWPIB in feed (Elder, 1982).

In a 2–year chronic toxicity study of LMWPIB in Charles River rats, four of the 30 males receiving 20,000 ppm in feed developed hematuria and three of these died during the first year (Elder, 1982). However, no pathologic changes were found to be statistically significantly associated with the dose of polyisobutene.

Iversen (1990) assessed potential carcinogenicity of LMWPIB (C12-C20) applied in acetone to the skin of *hr/hr* Oslo hairless mice and SENCAR mice twice weekly for 18 months. The potential of LMWPIB to promote tumors was also assessed using a single application of the tumor initiator 7,12-dimethylbenzanthracene (DMBA) followed by 18 months of application of isobutene in acetone. No effect on skin tumor formation was seen for LMWPIB applied with or without DMBA initiation. The report states that the number of malignant lymphomas and the number of lung tumors is statistically significantly increased in animals treated with LMWPIB by the dermal route. However, the statistical analysis is done using the number of tumors in both males and females and the tumor count in the PIB dose groups (20%, 40% and 80% PIB) is also summed before the statistical analysis is performed..

Combustion emissions

Combustion emissions were quantified from a diesel engine using CARB diesel fuel and from the same engine using Viscon diesel fuel. When Viscon fuel was used, particle emissions per horsepower hour were 27% lower than when CARB fuel was used. When Viscon fuel was used, emissions of NOx were slightly greater (2% greater) as were volatile hydrocarbon emissions (4% greater).

Table 1. Average Levels of VOCs Listed as Toxic Air Contaminants in Combustion Emissions from CARB Diesel Fuel or VISCON Diesel Fuel in Pre-durability test[1]

Air Contaminant	Emissions using CARB Diesel Fuel (mg/hp-hr)	Emissions using VISCON Diesel Fuel (mg/hp-hr)	Relative Change[2] (%)
Benzene	**0.009026**	0.012948	**+43**
Toluene	0.004228	0.006040	+43
Ethylbenzene	0.001811	0.002109	+16
Acetaldehyde	0.007385	0.009281	+26
Formaldehyde	0.02725	0.03345	+23
Propionaldehyde	0.001332	0.001513	+14

[1] Data from ARB.

[2] Calculated as 100×(VISCON emission rate – CARB emission rate)/(CARB emission rate)

Table 2. Average Levels of VOCs Listed as Toxic Air Contaminants in Combustion Emissions from CARB Diesel Fuel or VISCON Diesel Fuel in Post-durability Test[1]

Air Contaminant	Emissions using CARB Diesel Fuel (mg/hp-hr)	Emissions using VISCON Diesel Fuel (mg/hp-hr)	Relative Change[2] (%)
Benzene	**0.009026**	0.009237	**+2**
Toluene	0.004228	0.005016	+19
Ethylbenzene	0.001811	0.002465	+36
Acetaldehyde	0.007385	0.006948	-6
Formaldehyde	0.02725	0.03025	+10
Propionaldehyde	0.001332	0.001090	-18

[1] Data from ARB

[2] Calculated as 100×(VISCON emission rate – CARB emission rate)/(CARB emission rate)

Screening risk assessment for carcinogenic substances in diesel exaust

The amount of the carcinogenic TACs, acetaldehyde, benzene, ethylbenzene and formaldehyde, produced by an engine burning Viscon fuel in pre-durability tests is greater than the amount of these substances produced by the same engine burning CARB fuel. To assess potential impacts on human health from a substitution of Viscon fuel for a portion of CARB fuel, OEHHA scientists assumed that, for a carcinogenic substance in air, the cancer risk attributable to the substance is equal to the carcinogenic potency multiplied by the average ambient air concentration of the substance. With this assumption, an upper-bound estimate of the increase or decrease in cancer risk resulting from a substitution of Viscon fuel for a portion of CARB fuel is produced by the expression,

$$Risk = [C_{ambient}] \times [(A_P - A_C)/A_C] \times [E_d/Et] \times P \times F_m$$

Where,

$C_{ambient}$ is the average ambient outdoor air level of the carcinogenic substance,

A_P and A_C are the amounts of the substance produced per horsepower-hour by engines burning Viscon fuel and CARB fuel, respectively,

E_d is the estimate of the total releases per day of the substance from diesel vehicles and E_t is the estimate of releases into the atmosphere per day from all anthropogenic sources,

F_m is the maximum market share of Viscon fuel (chosen to be 0.2 per cent in accordance with ARB’s estimate),

P is the upper-bound estimate of carcinogenic potency in units $(\mu g/m^3)^{-1}$.

For a bounding estimate on risk, data were selected from the region of California with the highest ambient levels and the largest estimates of releases of these substances. This region is the South Coast Air Quality Management District (SCAQMD). Data from the Burbank monitoring station, which had the highest average concentrations, were used.

From estimates of E_d and E_t provided by ARB, the ratio E_d / E_t is calculated to be 16%, 11% and 1.8%, for acetaldehyde, formaldehyde and benzene, respectively. The estimate provided by ARB for the ratio of Viscon diesel fuel consumption to total diesel fuel consumption is 0.2%.

Table 3. Upper-bound estimates of lifetime cancer risks attributable to Viscon diesel fuel combustion emissions calculated from pre-durability test data in Table 1 assuming that 0.2 per cent of diesel engine fuel combustion is Viscon (calculated using ARB air monitoring data for 2002)

Chemical	Average Ambient Air Concentration ($\mu g/m^3$)	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$	Upper-Bound Lifetime Risk Increase Attributable to Substance in VISCON Diesel Emissions
Acetaldehyde	3.6	2.7×10^{-6}	6.0×10^{-10}
Formaldehyde	6.7	6.0×10^{-6}	1.3×10^{-9}
Benzene	3.2	2.9×10^{-5}	8.1×10^{-10}

Table 4. Upper-bound estimates of lifetime cancer risks attributable to Viscon diesel fuel combustion calculated from emission changes in the post-durability test data in Table 2 assuming that 0.2 per cent of diesel engine fuel combustion is Viscon fuel (calculated using ARB air monitoring data for 2002)

Chemical	Average Ambient Air Concentration ($\mu g/m^3$)	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$	Upper-Bound Lifetime Risk Increase Attributable to Substance in VISCON Diesel Emissions
Acetaldehyde	2.7	2.0×10^{-6}	4.5×10^{-10}
Formaldehyde	6.1	5.4×10^{-6}	1.2×10^{-9}
Benzene	2.3	2.1×10^{-5}	5.8×10^{-10}

Tables 3 and 4 list upper-bound screening estimates of lifetime cancer risk that might result from substituting Viscon fuel for 0.2 per cent of diesel fuel combusted in an air basin. These estimates are calculated from the pre-durability combustion test results in Table 1 because emissions of acetaldehyde, formaldehyde and benzene using Viscon diesel are higher than emissions using Viscon in the post-durability test. All estimates are below the widely used screening level of 10^{-6}.

The impact on average ambient levels of the respiratory irritants acetaldehyde and formaldehyde appears to be small when Viscon diesel fuel combustion is limited to 0.2% of diesel fuel combustion. Using the emissions data from the pre-durability tests, increases in average ambient levels of these aldehydes are predicted to be less than 0.01%.

The estimates of *Et* used for risk calculations do not include biological sources or formation by atmospheric chemical reaction. For acetaldehyde and formaldehyde, these processes are major components of the total amount added to the atmosphere per day. Inclusion of biological and atmospheric production to the estimate of E_t for these aldehydes would further reduce the corresponding upper-bound risk estimates.

Environmental fate of HMWPIB

No method quantifying the concentration of HMWPIB in any medium has been identified, and no studies of persistence of HMWPIB have been located. Furthermore, no reports of degradation products of HMWPIB have been found. It is therefore assumed in the following screening evaluation of environmental fate that HMWPIB may break down very slowly in the environment.

HMWPIB is not volatile and therefore would be present in particulate matter when released into air. Consequently, most HMWPMB in air would be deposited on soil and surface water.

HMWPIB released into water will not dissolve or evaporate to a significant extent. It will adsorp to particles containing organic matter if present and may accumulate in aquatic sediment.

HMWPIB released on soil or underground will bind strongly to organic substance in soil. It will remain where it binds unless soil is mobilized by wind, surface water flow or other process. HMWPIB resuspended by water flow may accumulate in aquatic sediments.

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APPENDIX E

Department of Toxics Substances Control: Recommendation on Proposed Viscon-Treated Diesel

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Department of Toxic Substances Control

Linda S. Adams
Secretary for
Environmental Protection

Maziar Movassaghi
Acting Director
1001 "I" Street
P.O. Box 806
Sacramento, California 95812-0806

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Multimedia Working Group
Air Resource Board

FROM: Li Tang, Ph.D. P.E.
Multimedia Products Section

Yun Zhang, PG
Geological Support Branch

VIA: Caroline Rudolph
Multimedia Products Section
Toxics in Products Branch

DATE: November 23, 2009

Subject: DTSC Recommendation on Proposed Viscon Diesel

Viscon Diesel is being proposed as a strategy for reducing harmful emissions and promoting uniform combustion in diesel engines. Viscon California, LLC submitted an application to the Multi-Media Working Group (MMWG) for evaluation, including a set of three-tier reports and attachments. As members of the MMWG, the Department of Toxic Substances Control (DTSC) staff reviewed the application and is providing the following comments and scientific recommendation:

Comments:

The active component of Viscon Diesel is an ultra-high molecular weight polyisobutylene (PIB). Viscon Diesel is manufactured in two steps: PIB is first dissolved into a California Air Resource Board (CARB) Diesel at a 1:99 (w/w) ratio to form a steady additive; then, the additive is blended into the CARB Diesel up to 500 ppm as a final product.

Emission testing demonstrated that the use of Viscon Diesel can reduce particulate air pollution. Information provided by the BASF Corporation (see Viscon Diesel Tier 1 Report, Attachments 1 and 2) indicated that the high molecular weight PIB has very low toxicity and is inert to most chemicals. Other properties of PIB are: it is completely insoluble in water; has high viscosity; and, has very low permeability.

The manufacturing process of Viscon Diesel has been compared with CARB Diesel. No significant difference was found regarding incidental release scenarios, waste management, or potential threat to human health and the environment. However, since diesel itself is toxic, there is no information to demonstrate whether the addition of PIB in diesel adversely impacts the cleanup of diesel in soil/groundwater when Viscon Diesel is incidentally spilled. It is necessary to conduct laboratory or pilot tests in order to complete the life cycle risk assessment of the new fuel, which the company Viscon California LLC has agreed to perform.

Recommendation:

After reviewing the Viscon Diesel application, DTSC conditionally supports the Viscon Diesel application due to its air emission reduction and low-toxicity of the PIB additive. As presented in its Tier III report, laboratory tests on biodegradation and soil-column fate-and-transport need to be conducted within one year to fill the knowledge gap. Therefore, DTSC recommends that the Environmental Policy Council conditionally approve Viscon Diesel pending submittal of the laboratory test results on biodegradation and fate/transport.

Should you have any questions, please contact Li Tang at ltang@dtsc.ca.gov or (916) 322-2505 or Yun Zhang at yzhang@dtsc.ca.gov or (916) 255-3700.

APPENDIX F

Letter of Conditional Approval of Tier I and Tier II dated May 19, 2009 and November 24, 2009

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Air Resources Board

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Linda S. Adams
Secretary for Environmental Protection

Arnold Schwarzenegger
Governor

May 19, 2009

Mr. Michael J. Porter
Viscon California, LLC
3121 Standard Street
Bakersfield, California 93308

Dear Mr. Porter:

Under the *Verification Procedure, Warranty and In-Use Compliance Requirements for In-Use Strategies to Control Emissions from Diesel Engines* (Verification Procedure), your Viscon™ fuel additive must undergo a multimedia evaluation pursuant to California Health and Safety Code section 43830.8. Based on its evaluation of the multimedia evaluation Tier I and Tier II reports you submitted for this fuel additive, the Multimedia Working Group believes these reports merit conditional approval, subject to the conditions described below, which would allow Viscon California to proceed immediately to Tier III of the multimedia evaluation process.

The conditional approval notwithstanding, the Multimedia Working Group identified the following knowledge gaps in the Tier I and Tier II reports (dated October 24, 2008 and April 28, 2009, respectively), which are incorporated herein by reference:

- The fate and transport of the Viscon additive and Viscon additive-treated diesel in soil compared to California diesel fuel (CARB diesel without the Viscon additive) in soil. This data gap includes, but is not limited to, the biodegradability of Viscon additive in soil.
- The impacts of the Viscon additive and Viscon-treated diesel on soil cleanup.

Based on your verification application and our discussions with you, we expect the Viscon fuel additive will have limited uses. Our expectation is based on the following:

- The Viscon fuel additive is 1 part ultra high molecular weight polyisobutylene and 99 parts CARB diesel.
- The Viscon fuel additive is used at a dose level in diesel of about 500 ppm. After receiving verification, the expected statewide consumption of Viscon additive and Viscon-treated diesel is about 3,650 gal/year (10 gal/day) and about 9.34 million gal/year, respectively.
- The Viscon fuel additive is not currently stored in underground storage tanks.

Although there are knowledge gaps in the Tier I and Tier II reports, the Multimedia Working Group finds that, even with these knowledge gaps, the potential risks to public health and the environment are minimal and acceptable, based on the expected limited use of the Viscon additive in California diesel fuel and information contained in the verification application.

As noted, this approval of the Tier I and Tier II reports is conditional and shall be rescinded if Viscon California fails to meet the following requirements to the satisfaction of the Multimedia Working Group:

1. Knowledge gaps pertaining to fate, transport, biodegradation, and potential soil cleanup impacts of Viscon and Viscon treated diesel have been identified. To address these gaps, Viscon California must meet all the following requirements (the Multimedia Working Group highly recommends that you work with an expert technical consultant to provide this information).

    a. Laboratory tests for biodegradability and fate and transport in soil is to be completed and the resulting reports to be submitted to ARB as soon as possible but no later than one year of the date of this conditional approval.

       Before conducting fuel tests Viscon California shall submit a test plan that describes the test objective and protocol to the Multimedia Working Group for approval. Again, the Multimedia Working Group highly recommends that you work with an expert technical consultant to develop this test plan.

    b. Information on potential impacts on soil cleanup is to be provided as soon as possible but no later than one year of the date of this conditional approval.

       Based on fate and transport results Viscon California shall submit a technical report that illustrates Viscon's potential impact on different soil cleanup methods. Again, use of an expert technical consultant for this effort is highly recommended.

   Please note that the information provided within the time period specified above may or may not be included in the evaluation that is to undergo scientific peer review and final determination by the Environmental Policy Council, depending on when the information is submitted to ARB.

2. For the aforementioned time period, conditional approval of the Tier I and Tier II reports is granted for the purpose of allowing the applicant to proceed to the Tier III phase of the multimedia evaluation process while allowing the applicant more time to provide additional data to fill in the knowledge gaps identified above.

3. In the event that these requirements are not met within the specified time, or the requested information, studies, or other relevant available information indicate significant risks to public health or the environment, the multimedia evaluation will be re-examined by the Multimedia Working Group and appropriate action determined.

4. Viscon and Viscon-treated diesel may only be stored in underground storage tanks that are in compliance with state and federal regulations as determined through the local agency with jurisdiction over the proposed storage site(s).

5. Viscon California, LLC shall provide quarterly reports the first year of receiving verification and annual reports thereafter.

6. Our findings regarding potential risks are based, in part, on the expected volumes of statewide consumption for your fuel additive. For annual sales greater than a specified volume threshold, to be determined by staff of the Office of Environmental Health Hazard Assessment (OEHHA), the Multimedia Working Group will re-examine the multimedia evaluation and identify any significant potential adverse impacts. Additional information and studies may be required based on OEHHA's analysis, and a re-evaluation of the potential risks may be warranted.

If you have any questions or comments, please contact me at (916) 327-5986 or by email at fvergara@arb.ca.gov, or Ms. Aubrey Sideco, Air Resources Engineer at (916) 323-7227 or by email at asideco@arb.ca.gov.

Sincerely,

/s/ by FV

Floyd Vergara, Esq., P.E.
Manager, Industrial Section

cc: Ms. Aubrey Sideco
Air Resources Engineer
Industrial Section

Air Resources Board

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Linda S. Adams
Secretary for
Environmental Protection

Arnold Schwarzenegger
Governor

November 24, 2009

Mr. Michael J. Porter
Viscon California, LLC
3121 Standard Street
Bakersfield, California 93308

Dear Mr. Porter:

Your request for a time extension to complete the requirements specified in the May 19, 2009 letter has been received. Due to the time required for the review and approval of the testing protocol, the deadline has been extended to <u>November 19, 2010</u>.

The deadlines specified in sections 1a and 1b of the May 19, 2009 letter have been amended as follows:

As noted, this approval of the Tier I and Tier II reports is conditional and shall be rescinded if Viscon California fails to meet the following requirements to the satisfaction of the Multimedia Working Group:

1. *Knowledge gaps pertaining to fate, transport, biodegradation, and potential soil cleanup impacts of Viscon and Viscon treated diesel have been identified. To address these gaps, Viscon California must meet all the following requirements (the Multimedia Working Group highly recommends that you work with an expert technical consultant to provide this information).*

    a. *Laboratory tests for biodegradability and fate and transport in soil is to be completed and the resulting reports to be submitted to Air Resources Board (ARB) by <u>November 19, 2010</u>.*

    Before conducting fuel tests Viscon California shall submit a test plan that describes the test objective and protocol to the Multimedia Working Group for approval. Again, the Multimedia Working Group highly recommends that you work with an expert technical consultant to develop this test plan.

    b. *Information on potential impacts on soil cleanup is to be provided by <u>November 19, 2010</u>.*

> *Based on fate and transport results Viscon California shall submit a technical report that illustrates Viscon's potential impact on different soil cleanup methods. Again, use of an expert technical consultant for this effort is highly recommended.*

Please note that the information provided within the time period specified above may or may not be included in the evaluation that is to undergo scientific peer review and final determination by the Environmental Policy Council, depending on when the information is submitted to ARB.

As requested, the deadlines specified in the May 19, 2009 letter have been amended. Please note that the remaining conditions and requirements outlined in the May 2009 letter remain the same.

If you should have any questions, please feel free to contact me at (916) 327-5986 or by email at fvergara@arb.ca.gov, or Ms. Aubrey Sideco, Air Resources Engineer, at (916) 324-3334 or by email at asideco@arb.ca.gov.

Sincerely,

/s/ by FV

Floyd Vergara, Esq., P.E.
Manager, Industrial Section

cc: Ms. Aubrey Sideco
Air Resources Engineer
Industrial Section

APPENDIX G

Biodegradation and Environmental Fate Testing Final Report

Effect of Fuel Additive Viscon on the Environmental Fate of Diesel Fuel
Department of Crop and Soil Sciences, University of Georgia

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Effect of Fuel Additive Viscon on the Environmental Fate of Diesel Fuel

Principal Investigators

Sayed M.Hassan, Ph.D.

Senior Research Scientist and Director
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University of Georgia
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To be Submitted to:

The California Environmental Protection Agency

Through:
VISCON CALIFORNIA, LLC
3121 Standard Street
Bakersfield, CA 93308

Final Report
Revised
January 3, 2011

TABLE OF CONTENTS

I. GENERAL INTRODUCTION

Diesel fuel consists of approximately 75% alkanes and 25% aromatics (Kostecki and Calabrese, 1992). The alkanes usually consist of a mixture of linear, branched and cyclic compounds. The aromatic fraction usually contains benzene, toluene, ethylbenzene and xylenes (BTEX) compounds and polyaromatic compounds (PAHs) in addition to others.

Viscon is an additive for diesel fuel which is being proposed as a strategy for reducing PM and NOx emissions for diesel engines. The active component of Viscon is an ultra high molecular weight polyisobutylene (UHMWPIB) polymer. Viscon is used at less than 5 ppm UHMWPIB to the end use CARB diesel. UHMWPIB is a non-toxic, colorless, tasteless, odorless food grade hydrocarbon polymer, which is insoluble in water. Lower molecular weight polyisobutylene (PIB) is a component in PIB amine keep-clean additives for gasoline. The use of Viscon as an additive to CARB diesel create no additional risks to the environmental or to human health when compared to unmodified CARB diesel. As an additive to diesel fuel it can result in a significant reduction in PM and NOx emissions from diesel engines (Las Palmas, 2008).

Knowledge gaps pertaining to fate, transport, biodegradation and potential soil cleanup impacts of viscon-treated diesel have been identified by the Multimedia Working Group of California Environmental Protection Agency. To address these gaps, laboratory tests for biodegradability and fate and transport in soil must be carried out. In addition, information on potential impacts on soil cleanup must be provided.

The literature refers to certain patterns by which biodegradation of different diesel components takes place. Saturated normal alkanes are the most readily degraded in a mixture (Atlas,1981; Bossert and Bartha, 1984). Lower molecular weight compounds are preferentially used by microbes (Chaineau *et al.,* 1995), but there is evidence that n-alkanes up to C44 have undergone microbial degradation (Atlas, 1981). In one batch study using a mixture of linear and branched alkanes, the linear alkanes were degraded fastest with the highest yield (Geerdink *et al.,* 1996). The branched alkanes were not consumed until most of the linear alkanes disappeared. Methyl branching and substitution generally increases the resistance of hydrocarbons to microbial attack (Atlas, 1981: Chaineau *et al.*, 1995). One study found that the degradation rate of branched alkanes was 2 times lower than n-alkanes (Chaineau *et al.*, 1995). However, there is some evidence that suggests that degradation of substituted cyclic alkanes occurs more readily than unsubstituted forms (Atlas, 1981). Compound classes in order of decreasing susceptibility to biodegradation are n-alkanes > branched alkanes > low molecular weight aromatics > cyclic alkanes. In one study, branched alkanes all degraded readily on their own, but when introduced as a mixture, degradation proceeded more slowly. This suggests a competition effect in mixtures (Kampbell and Wilson, 1991). On the contrary, there is much evidence, suggesting that for some compounds degradation is more rapid when present in a mixture than individually (Smith, 1990).

The object of this study is to design and carry out laboratory tests needed to address the knowledge gaps identified by the California Environmental Protection Agency Multimedia Working Group. Sets of experiments were carried out to determine whether addition of Viscon at the recommended concentration would significantly affect the environmental impact of diesel fuel spills in soils, and whether such additives would change potential remediation approaches to such spills. In this respect, study of the impacts of the additive on soil microbial growth and consumption of diesel constituents is of prime importance since aerobic bioremediation is the method of choice in remediating oil spills. Of equal importance is the flow capacity of the soil since during a remediation process, flow rate of spilled diesel through soils has an important impact on remediation. The first objective was studied by setting up incubators of sandy loam soil impregnated with untreated and Viscon treated diesel at 5% concentration range over a period of several months. During that time periodic analysis of carbon dioxide in the headspace and diesel hydrocarbon content of the soil were carried out. The results obtained from this simultaneous and paired testing were statistically refined to exclude outliers using Q-test (Dean and Dixon, 1951; Rorabacher, 1991) and then subjected to paired *t*-test (Paired t-test Using Microsoft Excel) to evaluate the significance of the difference between the Viscon spiked and unspiked diesels. The second objective was studied by running a series of paired column studies prepared using the same soil in the air-dry state and with moisture content of 15%. The same statistical approach was applied to investigate if inclusion of Viscon at the 5 ppm concentration results in a real difference in the flow of diesel in the soil columns.

I. IMPACT OF VISCON ON DIESEL BIODEGRADATION

1. Introduction:

The main technologies for remediation of oil contaminated soils are based on either physical, chemical or microbiological methods. Physicochemical methods are selective for groups of the complex contaminant (Morgan and Watkinson, 1989) and include thermal, extraction, oxidation, flooding, adsorption and immobilization. The inclusion of Viscon at the 5 ppm range should not be expected in any way to impact the harsh physicochemical remediation techniques of diesel. The decontamination of soils by microbiological means has been established as efficient, economic and versatile (Bartha, 1986; Bluestone, 1986). Due to the highly sensitive nature of microbial growth and liability of remediation techniques derived there from, it is necessary to study the impact of low concentration of chemical additives on its microbiological remediation. In this respect, two indicators for diesel degradation were examined: (1) generation of carbon dioxide and (2) content of diesel range hydrocarbons. The latter measure was studied through TPH and follow up of C12 to C24 straight chain hydrocarbons.

2. Soil Preparation:

The soil used in these experiments was sandy loom obtained from the Research Station, University of Georgia. Prior to use, it was air dried and sifted through a 2 mm sieve and subsequently placed in sealed plastic container for storage. Table (1) shows some of the physical and chemical properties of the soil.

Table 1. Some Physicochemical Properties of the Selected Soil:

Soil pH:	5.26
Soil Moisture Content	1.92%
Particle size distribution**:**	
Clay	10.5%
Silt	13.5%
Sand	76.0%
Elemental analysis:	
Soil Total organic carbon	0.336%
Soil Total Carbon (TC)	1.135%
Soil Inorganic carbon	0.799%
Soil Total Nitrogen	0.052 %
Soil Extractable Phosphorous	6.3 mg/k

Nutrient addition was required to adjust the C:N:P ratio to 200:10:1 to maximize microbial growth (Zynter at al, 2000). Ammonium nitrate and potassium dihydrogen phosphate were used as sources of nitrogen and phosphorous at levels when 1 – 5 ml added would result in the desired C:N:P ratio.

Figure 1. Incubation set up for control soil, diesel contaminated and Viscon treated diesel contaminated soil samples.

3. Soil Incubation:

Aliquots of 500 g of the soil were transferred to new cleaned quart Mason jars. Twenty five ml of regular diesel were added to each of six jars and 25ml of Viscon treated diesel (V.T. Diesel) were added to each of another six jars; 2 jars were left with soil only as control. The jar contents were thoroughly mixed and placed in a cooler over night. 10ml of growth nutrient was added to the quart jars, thoroughly mixed and kept covered air tight with neoprene stoppers fitted with 2 mm Teflon liners to mitigate the effects of diesel fuel on the stoppers. Each stopper was drilled with two holes; one to accommodate glass tubing fitted with screw capped 11 mm rubber septum at the top to act as a port through which gas samples for GC analysis can be withdrawn and through which oxygen replenishment of the incubators can take place. The second hole was meant to contain an upright copper tubing that reaches the bottom of the headspace close to the soil surface. The top part of that tube is connected through flexible rubber tube to the top of a 9 inch glass Pasteur pipette that has been dipped through its narrow end under the surface of 1N sodium hydroxide solution contained in 250 ml Erlenmeyer flask with a side arm blocked with thick layer of parafilm. The whole setup as shown in fig. 1 is kept airtight closed to prevent the escape of carbon dioxide or hydrocarbon gases.

In order to avoid consumption of the oxygen in the headspace and creation of anaerobic environment, replenishment of the consumed oxygen -as indicated by headspace analysis- was done by passing pure cylinder oxygen in the system. In order to achieve a more or less equal share of oxygen to each incubator, a tubing manifold was designed starting from one single metal tube connecting the oxygen regulator to a series of flexible branching smaller tubes of equal length each reaching the base of wide bore #2 syringe needle. Each needle was inserted through the rubber septum port into each of the 14 incubators. The rate of gas flow to each incubator was indicated by the bubbling rate in the sodium hydroxide reservoirs and was kept at a moderately low pressure but at equal pace using flow restrictors fitted at the entrance of each incubator. Our experiments indicated that a flow of gas at 30 psi for up to one hour resuled in more than 15% of oxygen saturation in the headspace. Trials made to pass air current instead of the cylinder oxygen failed to supplement enough oxygen in a reasonable time (few hours) and can lead to inevitable loss of hydrocarbons. The same drawback applies to the widely used technique of incubator aeration opening and soil mixing in open atmosphere.

During the study, the 14 incubators were left at room temperature (about 70 ± 5 degrees F). Gas samples from the headspace for carbon dioxide and oxygen analysis were carried out 2 times a week while soil samples for single hydrocarbon and total petroleum hydrocarbons analyses were collected every 3 weeks. Table 2 shows the time change of carbon dioxide concentration in the headspace.

II. IMPACT ON CARBON DIOXIDE FORMATION:

1. Instrumental parameters:

A HP6890 series gas chromatograph (GC) (Agilent Technologies, Wilmington, DE 19808) supplied with an electronic pneumatics control (EPC) injector, thermal conductivity detector (TCD), and data processing unit was used. The inlet temperature, in the splitless mode, was kept at 150^{o}C and pressure at 5.32 psi with helium as the eluent and reference gas; total gas flow was 76.4 ml per minute. The oven Initial temperature was kept at 50 ^{o}C for 1.00 min then ramped at a rate of 25^{o}C per minute to reach 100^{o}C then a second ramp of 30^{o}C per minute to 200 ^{o}C and kept at this temperature for 4 minutes; total run time: 10.33 min. The HP PLOT molesieve column (Agilent Technologies, Wilmington, DE 19808) was used for the separation; column length:15 m, internal diameter: 0.53 mm, film thickness: 50 um.

Manual injection of the samples was done using 3 ml Gas-Tight Syringes supplied with Teflon Luer lock valve Fitting. Before sample withdrawal, the syringe is filled and evacuated into the incubator headspace for 10 times to mix the gas and get an aliquot representative to the whole headspace. Instrument calibration was done using standard 5% carbon dioxide in nitrogen (Supelco).

2. Results:

Table 2 shows the concentration of carbon dioxide in the headspace of the incubators calculated in microliter amounts for both the untreated and the Viscon treated diesels.
In order to assess the difference between the mean values of the two sets of carbon dioxide results, paired ***t***-test of statistical analysis was applied; the results are shown in Table 3. As evident from table 3, both the calculated one-tailed and two-tailed values of ***t*** were less than the relevant critical values. Accordingly, the noticed difference between the means of the two data sets is statistically non significant and that addition of Viscon has no effect on carbon dioxide formation during aerobic biodegradation of the treated diesel. The same conclusion can be depicted from the histogram in Figure 2.

Table 2. Concentration of carbon dioxide in the bio-reactors headspace calculated in micro-liter amounts.

Analysis Date	Control	Diesel	V.T.Diesel
*3/25/2010	0.0	0.9	4.0
3/29/2010	5.6	11.6	20.4
4/1/2010	9.7	28.5	43.7
4/5/2010	15.1	67.8	84.0
4/8/2010	18.7	107.3	126.5
4/12/2010	19.4	161.8	147.2
*4/15/2010	3.8	36.6	30.4
4/19/2010	8.7	117.8	102.1
4/22/2010	12.0	117.3	123.3
*4/26/10	3.3	81.1	83.3
4/29/2010	5.8	122.1	143.2
5/3/2010	8.8	225.0	203.4
*5/6/2010	5.8	76.6	84.0
5/10/2010	13.6	125.2	179.7
5/13/10	11.9	130.3	167.8
5/17/2010	31.8	293.7	254.2
*5/20/2010	4.2	84.2	127.5
5/24/2010	35.1	283.9	299.8
*5/27/2010	5.6	81.0	82.0
*6/1/2010	10.4	167.3	189.6
6/3/2010	13.2	267.6	221.0
6/7/2010	26.0	279.0	225.1
6/10/2010	17.0	130.9	72.8
6/14/2010	21.9	181.2	134.8
Total	307.1	3,178.6	3,149.7

(*) Values measured after soil sampling for hydrocarbon analysis.

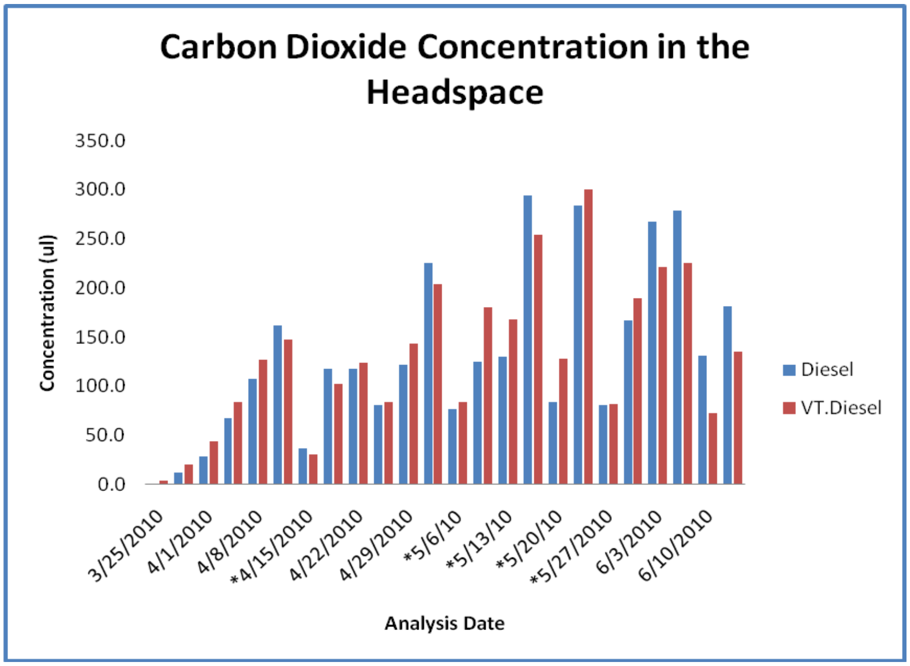

Figure 2. Comparison of carbon dioxide formation due to aerobic biodegradation of Viscon treated and none treated diesel by naturally occurring soil micro-organisms.

Table 3. Calculation of paired t-Test for the carbon dioxide results in Table 2.

	Diesel	*V.T.Diesel*
Mean	132.44	131.24
Variance	7380.43	5781.58
Observations	24	24
Pearson Correlation	0.9356	
Hypothesized Mean Difference	0	
df	23	
t Stat	0.1923	
P(T<=t) one-tail	0.4246	
t Critical one-tail	1.7139	
P(T<=t) two-tail	0.8492	
t Critical two-tail	2.0687	

IV. IMPACT ON HYDROCARBON CONTENT OF DIESEL:

1. Introduction:

Experiments to study this parameter were carried out every 3 weeks. In these experiments the incubators were carefully opened and the soils thoroughly mixed to be able to withdraw representative samples from each incubator. To avoid hydrocarbon loss, the extracting solvent (equal mixture of hexane and acetone) and necessary glass ware and other utensils must be prepared and ready to use. Two samples were withdrawn from each jar; one for total petroleum hydrocarbon (TPH) determination and another sample for diesel hydrocarbon content analysis. After finishing of sample collection, replenishment of nutrient solution was achieved by adding 5ml of a 100x solution to the jar content. The incubators were recapped, hooked together as previously explained in the setup and shown in figure 1. Cylinder oxygen was then passed through the incubators to ensure their aerobic nature and left for the next sampling activity.

2. Total Petroleum Hydrocarbons:

TPH samples were composite and consisted of equal parts from each of the relevant sample sets (Controls, Diesels and V.T. Diesels) and as such only 3 TPH extractions are performed every 3 weeks. Extraction was done in 40 ml screw capped, dark colored glass bottles. To one bottle, 20 ml of the hexane-acetone mixture was added followed by six 1g samples derived from the six diesel incubators. To another bottle six 1g samples representing the V.T. diesel incubators was prepared. The control composite was prepared using two 3g samples representing the 2 control incubators. This will result in exactly 6 grams of samples in each TPH bottle. Place the bottles in the ultrasonic bath for an hour; make sure the water level in the bath comes to just above the solvent level. Remove the bottles from bath and release pressure by uncapping for 2 seconds, recap and allow cooling to ambient temperature. Centrifuge for 20 minutes at 1600 RPM. Label, pre-weigh and record the weights of three 125ml Erlenmeyer flasks to 3 decimal places. After centrifugation, pour the solvent mix into the labeled Erlenmeyer flasks. Re-extract the soil by adding 15ml solvent to each bottle, ultrasound for 30 minutes, centrifuge and add solvent to the relevant Erlenmeyer flask. This last step was repeated a second time for a total of 3 extractions. Place the flasks in the fume hood and allow the solvent to evaporate. Record the weight of the flasks and calculate the % residue left in each flask. This % residue represents the total hydrocarbon content of the extracted soil.

3. RESULTS:

Table 4 shows the results of TPH by time obtained under the incubation conditions of the study.

Table 4. Total Petroleum Hydrocarbon content of the incubated soils:

Date	Control	Diesel	VTDiesel
		% Residue	
3/23/2010	0.05	2.87	2.70
4/13/2010	0.03	2.12	2.13
5/4/2010	0.05	1.78	1.78
5/27/2010	0.18	2.75	1.90
6/15/2010	0.33	1.38	1.08

Subjecting the results in table 4 to paired comparison of statistical analysis revealed that the difference between the means of the TPH for both the diesel and the Viscon treated diesel incubated soils are not significantly different since the calculated t-value was less that the critical value. The t-test results are presented in table 5.

Table 5: t-Test: Paired Two Sample for Means

	Diesel	*V.T.Diesel*
Mean	2.01	1.73
Variance	0.334	0.204
Observations	4	4
Pearson Correlation	0.717	
Hypothesized Mean Difference	0	
df	3	
t Stat	1.399	
P(T<=t) one-tail	0.128	
t Critical one-tail	2.353	
P(T<=t) two-tail	0.256	
t Critical two-tail	3.182	

On the other hand, figure 3 shows a linear disappearance profile for the two incubated soils with the Viscon treated having a steeper rate than the untreated diesel. Since the data in figure 3 are the same used to calculate the paired t-test in table 5, it can be concluded that the difference in slope of the 2 lines is by chance or due to experimental error.

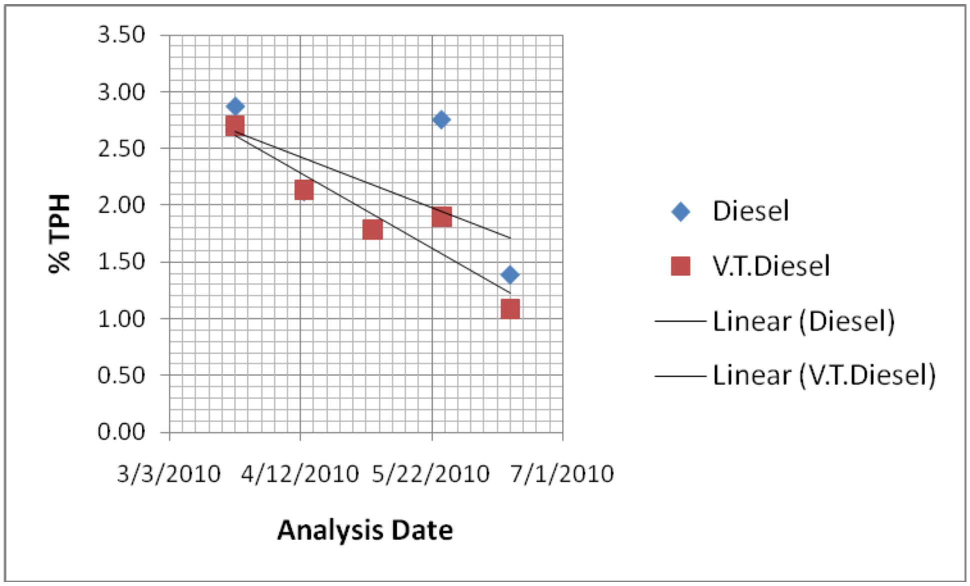

Figure 3: Change of TPH by Time for the incubated soils

VI. IMPACT ON INDIVIDUAL HYDROCARBONS:

Soil sampling for quantification of separate diesel hydrocarbons was carried out when sample jars are opened every 3 weeks for TPH sampling. Prior to opening jars, label fourteen 40 ml screw capped, dark colored glass bottles; one vial for each sample. Into each vial add 4g of anhydrous sodium sulfate (Fisher Scientific) followed by 10ml of methanol. When incubation jars are opened and ready for sampling, transfer exactly 1 gram from the soil and add it to the methanol in the corresponding amber vial and cap immediately. Place the vials in the ultrasonic bath for 1 hour, again making sure the water level is just above the solvent level. Centrifuge for 20 minutes at 1600 RPM and carefully transfer 1.5-2.0ml of the methanol into amber colored GC auto sampler vials. Samples were then analyzed using GC/MS for C12 to C24 hydrocarbons characteristic to the diesel fraction.

1. Instrumental Parameters:

Agilent 6890 gas chromatograph with a 5973 mass spectrum detector and equipped with an auto-sampler was used to analyze the samples. A 30 m, 0.32 mm ID J and W Scientific DB-5 capillary column with a 0.25 um film thickness was used. The oven program was held at 50°C for 1 min, before being ramped up to 260°C at 12°C/min and kept at that temperature for 12 min. The GC-MSD was calibrated using a three point linear regression curve developed by serial dilution of commercial available standard solution (Absolute Standards Inc.) containing a mixture individual compounds with methanol.

2. Results:

Table 6 shows the results of the 13 hydrocarbons from C12 to C24 obtained over the incubation time for the untreated diesel spiked soil. Table 7 shows VTDiesel spiked soil under the same conditions.

Table 6. Change of Hydrocarbon Concentration by Time During Incubation of Diesel Treated Soil.

Compounds	3/26/2010	4/16/2010	5/6/2010	5/27/2010	6/16/2010	Average
			Concentration, mg/kg			
Dodecane	102.7	100.9	208.1	133.4	86.7	**105.3**
Tridecane	92.7	113.2	156.2	105.8	87.5	**92.6**
Tetradecane	645.1	414.8	758.0	491.6	127.1	**406.1**
Pentadecane	448.4	380.1	569.5	110.8	80.3	**264.8**
Hexadecane	124.5	143.9	179.5	86.5	100.1	**105.8**
Heptadecane	223.8	274.4	256.6	145.6	83.5	**164.0**
Octadecane	109.5	130.4	139.3	76.6	69.0	**87.5**
Nonadecane	49.2	281.0	68.4	24.6	23.9	**74.5**
Eicosane	73.6	36.0	88.1	29.4	26.7	**42.3**
Heneicosine	0.9	1.2	0.7	del	0.5	**0.7**
Docosane	33.7	32.0	18.5	1.5	9.1	**15.8**
Tricosane	32.2	29.2	18.2	1.5	9.1	**15.0**
Tetracosane	12.5	14.3	31.7	8.6	10.8	**13.0**
Sub Totals	1948.7	1951.5	2492.8	1216.0	714.3	
Total	8323.4					

Tables 6 and 7 shows the average values of six determination for each of the 13 hydrocarbons characteristic of the diesel range in the incubated spiked soils with none treated and the Viscon treated diesels, respectively. Both tables show a decrease in the hydrocarbon content by time due to microbial action. Assessment of the difference between the results of tables 6 and 7 was done by comparing the mean values reported in the right hand column in each table using the paired t test of statistical analysis. As shown in table 8, the calculated t whether using the one-tail or two-tail test is less than the critcal value indicating that the difference between the 2 means is not statistically significant. The same conclusion was achieved by comparing the effect of the viscon additive on each of the measured thirteen hydrocarbons. Results of the latter comparison are appennded at the end of this report under Appendix 1.

Table 7. Change of Hydrocarbon Concentration By Time During Incubation of V.T.Diesel Treated Soil.

Compounds	**3/26/10**	**4/16/10**	**5/6/10**	**5/27/10**	**6/16/10**	**Average**
			Concentration, mg/k			
Dodecane	153.1	214.2	206.5	137.1	5.3	**119.4**
Tridecane	148.7	220.9	154.7	107.7	4.5	**106.1**
Tetrade cane	522.8	230.0	796.5	512.8	17.3	**346.6**
Pentadecane	487.5	161.5	585.7	86.0	11.1	**222.0**
Hexadecane	179.2	353.2	180.0	83.5	4.4	**133.4**
Heptadecane	219.7	205.8	255.2	146.2	9.9	**139.5**
Octadecane	128.4	200.2	145.3	77.7	4.0	**92.6**
Nonadecane	161.8	180.0	64.0	12.6	9.8	**71.4**
Eicosane	82.0	38.4	89.8	32.3	2.7	**40.9**
Heneicosine	0.8	0.8	0.8	7.8	0.1	**1.7**
Docosane	27.8	24.7	14.0	0.9	1.3	**11.5**
Tricosane	26.2	21.2	18.1	0.9	1.3	**11.3**
Tetracosane	17.4	25.9	30.1	7.4	0.9	**13.6**
Sub Totals	2155.4	1877.0	2540.6	1212.9	72.5	
Total	7858.4					

Table 8. Comparison of the Difference Between the Data in Tables 6 and 7 using the *t*-Test of Paired Comparison of Two Sample Means of Statistical Analysis.

	Diesel	*V.T.Diesel*
Mean	106.72	100.75
Variance	13365.02	9663.32
Observations	13	13
Pearson Correlation	0.9885	
Hypothesized Mean Difference	0	
df	12	
t Stat	0.909	
P(T<=t) one-tail	0.191	
t Critical one-tail	1.782	
P(T<=t) two-tail	0.381	
t Critical two-tail	2.179	

VI. IMPACT ON DIESEL RANGE ORGANICS (DRO):

From the qualitative point, It is evident from the chromatograms on pages 15 and 17 for diesel at the start and at the end of incubation, respectively. that diesel keeps its DRO profile. Addition of viscon did not affect that profile as evident from the chromatograms on pages 16 and 18. Yet the decrease in hydrocarbon concentration is reflected on the height of the y-axis for both diesels before and after incubation.

```
File        : D:\1\DATA\VISH326\DIESEL1.D
Operator    :
Acquired    : 26 Mar 2010  12:15 pm using AcqMethod OILSIM
Instrument  :   GC/MS Ins
Sample Name: Diesel_1
Misc Info   :
Vial Number: 4
```

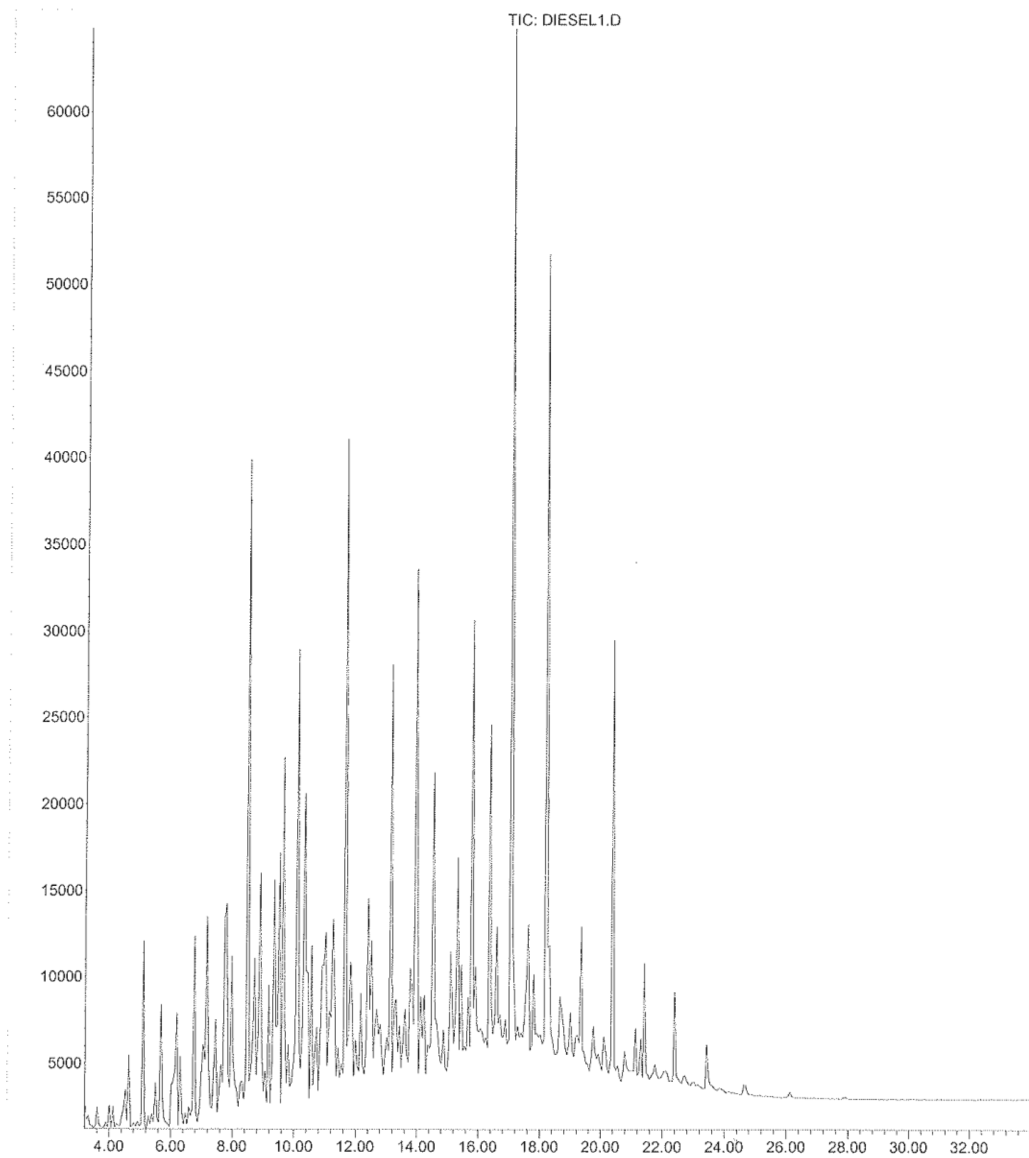

Figure 4. Diesel-range organic compounds as shown in gas chromatogram for untreated diesel at start of incubation experiment.

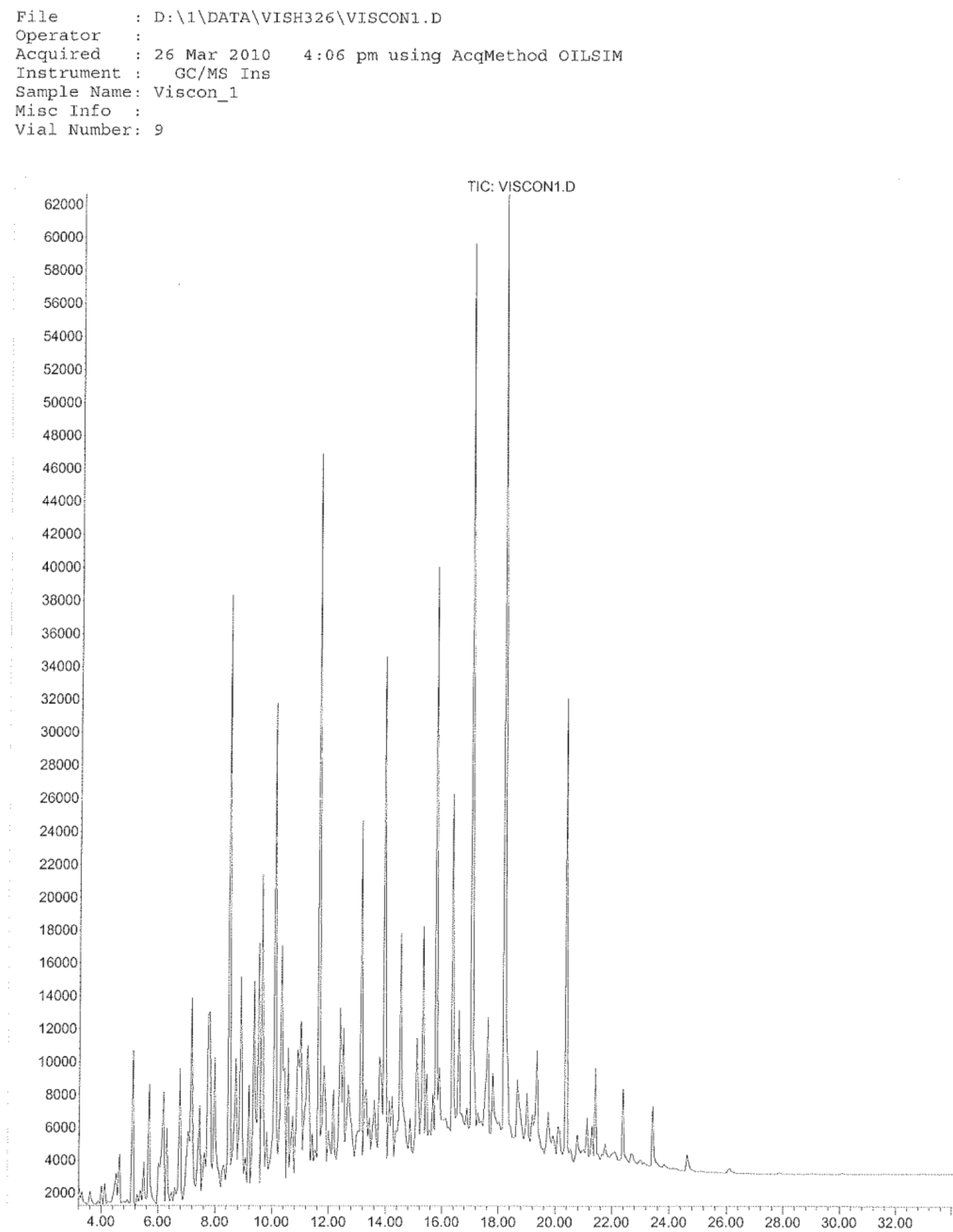

Figure 5. Diesel-range organic compounds as shown in gas chromatogram for Viscon- diesel at start of incubation experiment.

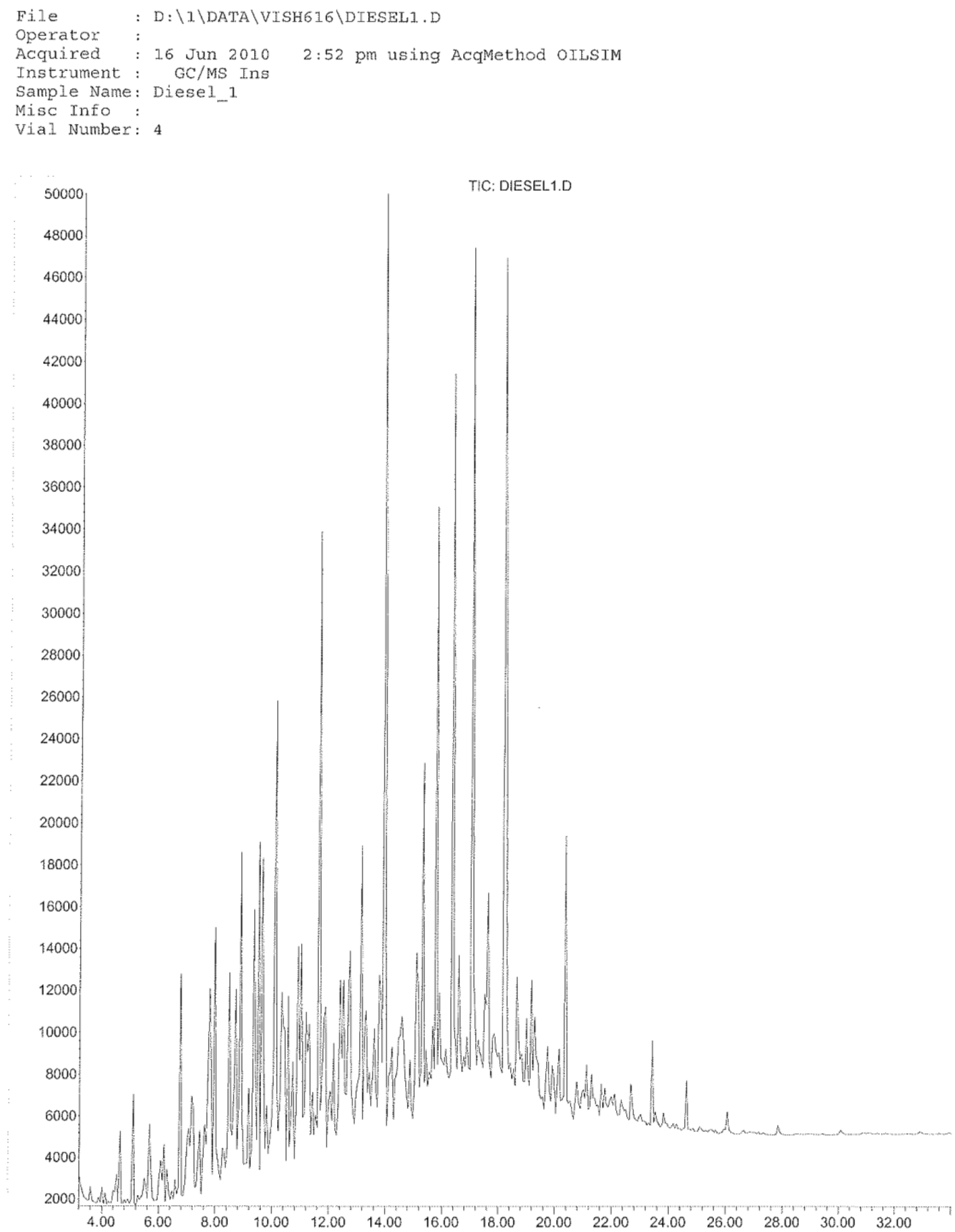

Figure 6. Diesel-range organic compounds as shown in gas chromatogram for untreated diesel at end of incubation experiment.

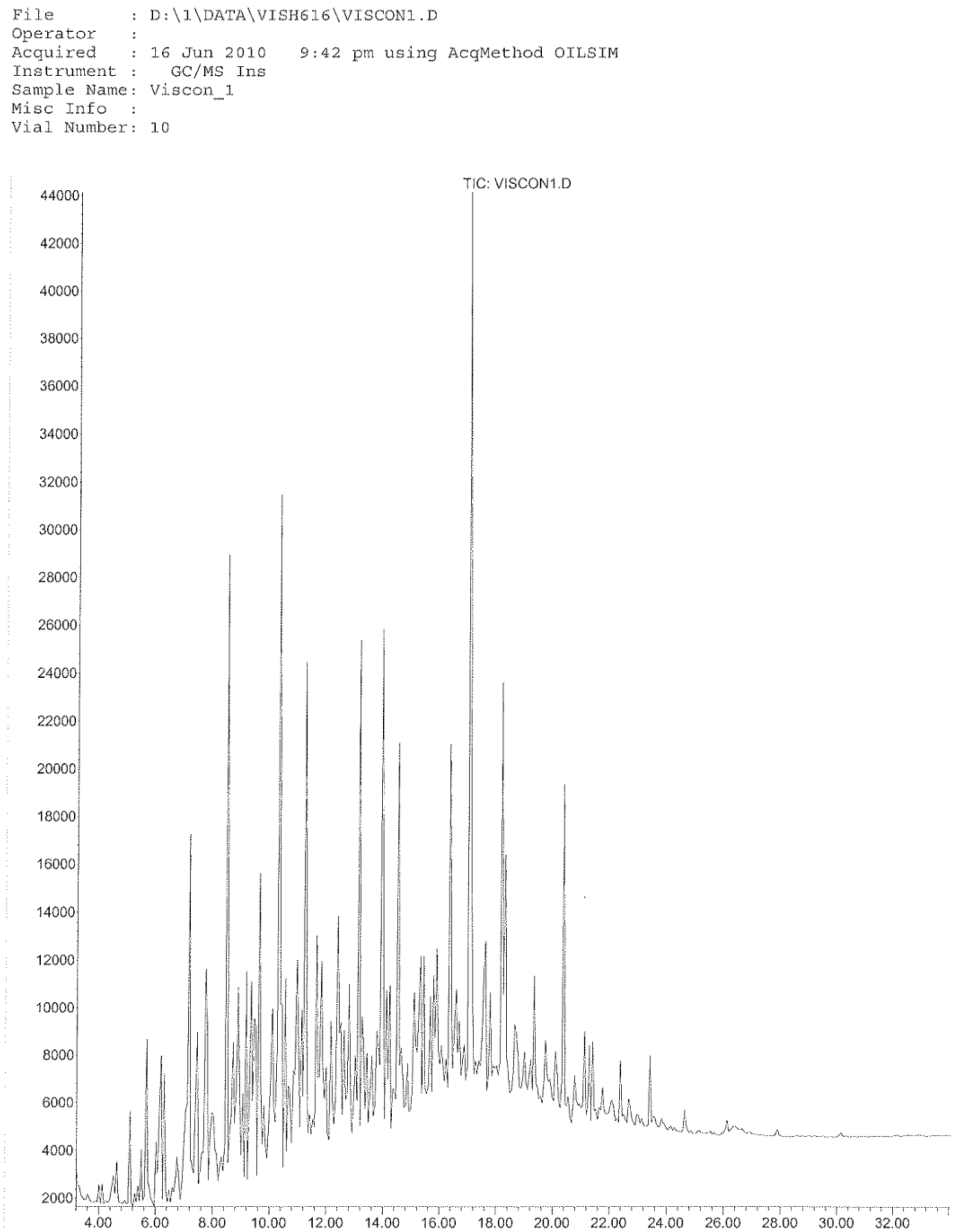

Figure 7. Diesel-range organic compounds as shown in gas chromatogram for Viscon-treated diesel at end of incubation experiment.

VII. FLOW OF VISCON-TREATED DIESEL FUEL THROUGH SOIL COLUMNS

The objective of this experiment was to determine the flow rate of Viscon-treated and untreated diesel fuels through repacked soil columns at two soil moisture contents. Flow rate is an important consideration in remediation of fuel spills, and it is desirable that fuel additives do not increase the rate of flow.

1. Methods

Glass columns (permeameters) 5 cm in diameter fitted with glass fritted outlets were used in this work. Soil (Cecil sandy loam, screened to < 2mm, initially air-dried to 3% (wt/wt) moisture) either used as-is in the “dry” soil experiments, or wetted to 15% total soil moisture (wt/wt) using deionized water and allowed to equilibrate in sealed containers in the lab for several weeks.

For the dry soil experiments, soil was packed into the columns using an orbital shaker to continually agitate the soil as it was slowly added to the column from the top (Figure 8). This resulted in a uniformly packed column approximately 20 cm in height with a bulk density of 1.5±0.05 g/cm^3 and an overall porosity of 43%. For the moist soil experiments, the moist soil was incrementally packed into the columns in 10 roughly equal “lifts” which were individually compacted using a plunger-type device. The bulk density of these columns was 1.32± 0.05 g/cm^3, computed using the dry soil mass and the column space occupied ($v = h \pi r^2$).

Figure 8. Packing dry (3%) soil columns

Total porosity was computed using

$$\rho = 1 - (BD/PD)$$

where BD is bulk density (g/cm^3), PD is particle density (assumed to be 2.65 g/cm^3), and ρ is total porosity, in this case equal to 0.50 (Brady and Weil, 2008)

Fuel materials (either CA-approved diesel fuel or Viscon-amended diesel, supplied by Viscon California LLC) were reported to have equal specific gravities (0.83) and viscosities (1.80 cP) by the supplier. Fuels were added to columns in individual experimental runs by adding to a funnel at the top of the column until a free head of 2.5 cm was achieved above the soil surface. This hydraulic height was maintained for the duration of the experimental run; the added fuel was observed to uniformly wet the soil mass in the column until saturation was reached, at which point fuel began to exit the column through the fritted outlet. For the dry soil runs, the columns were allowed to run for approximately 5 minutes, then timed aliquots of percolated fuel were collected and volumes measured at 10 minute intervals over the next 30 minutes. For the moist soils, diesel was run through the columns for 30 minutes before flow measurements were initiated. Flow rates (Q) were taken as averages of 3 sequential volume measurements.

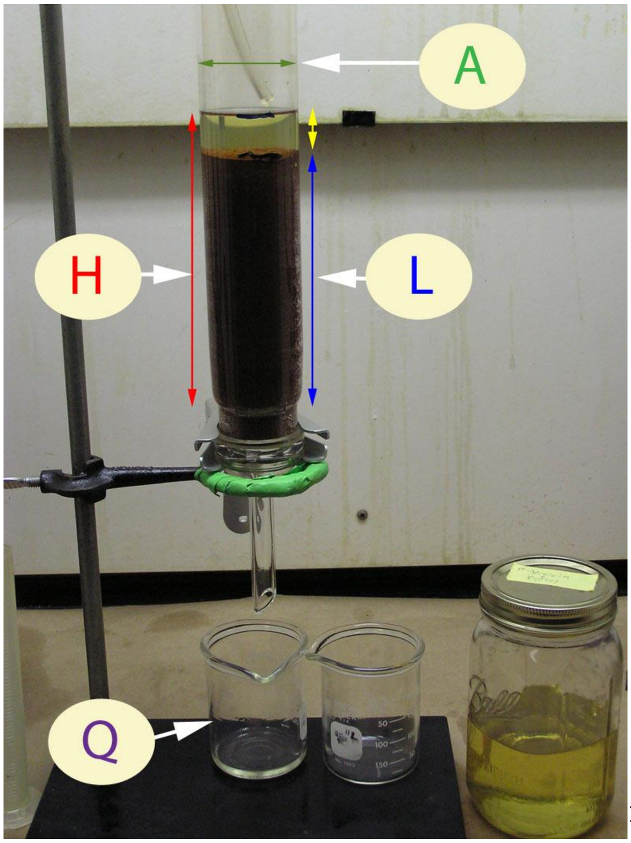

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Figure 9. Soil column in operation; yellow arrow is 2.5 cm head above soil surface; total head (red) is from fuel surface to outlet. See text for other symbols.

Darcy's Law was used to compute a saturated hydraulic conductivity (K_{sat}, cm/min) for the soil columns using each of the fuels:

$$Q = K_{sat} \times H/L \times A$$

where Q is the collected percolate volume (cm^3/min), H is the total hydraulic head (cm), L is the flow length (cm), and A is the column area (cm^2) (see Figure 9).

Four replicate columns were run for each diesel fuel at each moisture content. Mean values for final K_{sat} were compared using a two-tailed t-test at a 0.05 probability level, assuming equal variances. The critical t statistic for significance with 6 degrees of freedom was 2.44, meaning that the computed t must exceed this value for mean values to be considered statistically different with 95% confidence.

2. Results and Discussion

Dry (3% moisture) soil: Flow rates reached a steady state very rapidly in the dry soil columns, and the three measurements of volume taken were very similar. The results (see Table 9) showed a moderate amount of variability; the Viscon-treated fuel appeared to have a slightly lower K_{sat} (slower flow) through the dry soil, but the calculated t value (1.98) did not exceed the critical value of 2.44. Thus the difference between means was significant only at the 9.5% (0.095) level of probability, which is less than the 0.05 level normally used in such mean comparisons. The variation in values of K_{sat} obtained were likely due to small difference in column packing, which may have resulted in varying flow pathways for the fuels through the columns.

Moist (15%) soil: The moist soil packing was attempted with a variety of compaction techniques in an effort to obtain a uniform soil column. Too much compaction effort resulted in a stratified (layered) soil column that was clearly not uniform; the use of incremental "lifts" of soil somewhat alleviated this problem, but it was decided to use only a moderate compaction effort to minimize density stratification. The resultant columns had lower bulk densities and higher porosities than the dry soil, but densities were maintained at uniform levels among the replicate moist columns. Flow rates did not stabilize until about 30 minutes after initiation for the moist soil columns (Figure 10), and flow rates were overall much higher for the moist soil than the dry soil. It is assumed this was due to the lower bulk density and higher porosity of the moist soil columns, a result of the way the columns were set up and compacted. The moist soil was also clearly more aggregated, potentially resulting in larger pore sizes than the dry soil. Computed K_{sat} values for these columns (Table 10) taken after the initial flow period showed a greater column-to-column variability (coeff. of variation =16-31%) than the dry soil columns, a reflection of difficulties in packing moist soil. Mean K_{sat} of the diesel fuel here again appeared to be higher than the Viscon-treated fuel, but the computed t was significant only at the 16% level (0.163). Thus, at the normal 0.05 probability, the two mean values are not different from each other.

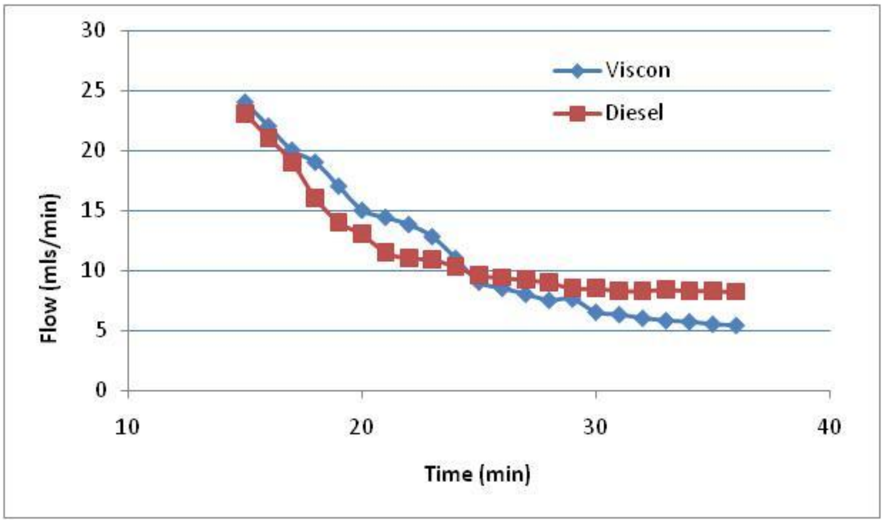

Figure 10. Flow rate (mLs/min) over time for two example columns using moist (15% moisture content) soil using diesel and Viscon-treated diesel fuels.

There is some likelihood that, with more replication and/or better control of packing densities in the columns, it might be shown that the Viscon fuel flows at a significantly slower rate than untreated fuel. This trend is apparent in the current data, but not sufficiently to result in a significant difference. It is possible that this potential difference would be related to the differences in fuel properties conferred by the Viscon additive; however, the fuels used were reported by the supplier to have essentially identical specific gravities and viscosities. The current data presented here, however, indicate the magnitude of any effect of such differences in properties is limited: in both dry and moist soil conditions tested, the Viscon-treated fuel K_{sat} values were about 30% lower than the regular diesel fuel. Even if these differences in flow velocity were statistically different, in a practical field situation such differences would not be likely to have a major impact on fuel migration rates through soils.

As a result, it is concluded that migration rates of fuel through soils (e.g., during a spill or leak) towards an aquifer would be similar for both types of fuels. This would imply that clean-up or remediation techniques (including excavation, extraction, biodegradation, or containment) would not be appreciably different if a Viscon-treated fuel were involved, as compared to a standard diesel product.

Table 9. Individual runs and statistics for diesel fuel runs (3% soil moisture)

	Diesel	Viscon
replicates	-----cm/min----	
1	0.098	0.056
2	0.067	0.058
3	0.067	0.049
4	0.058	0.056
mean	0.0726	0.0547
std. dev.	0.0176	0.0039
coeff. of variation (%)	24	7
t probability*	0.095	
computed t value*	1.98	

The probability gives the likelihood that the two mean values are from different populations (ie, are significantly different) based on the computed t value shown. Critical t = 2.44

Table 10. Individual runs and statistics for diesel fuel runs (15% soil moisture)

	Diesel	Viscon
replicates	-----cm/min----	
1	0.376	0.257
2	0.248	0.208
3	0.412	0.264
4	0.212	0.190
mean	0.312	0.230
std. dev.	0.0969	0.0362
coeff. of variation (%)	31	16
t probability*	0.163	
computed t value*	1.59	

The probability gives the likelihood that the two mean values are from different populations (ie, are significantly different) based on the computed t value shown. Critical t = 2.44

VII. CONCLUSIONS

In order to assess the effect of Viscon on biodegradation of diesel fuel, a series of laboratory studies were performed on sandy loam soil spiked with 5% (v/wt) regular diesel fuel and with 5% of Viscon treated diesel. The biological parameters monitored were (1) carbon dioxide formation, (2) total petroleum hydrocarbons, and (3) individual hydrocarbons. Based on the results obtained and the non-significance of the t-test for statistical comparison between the means of each study, it can be concluded that addition of Viscon to diesel at 5 ppm concentration does not affect the biodegradation of the spiked diesel. Moreover, the profile of diesel range organics (DRO) did not seem to be affected by addition of Viscon. This result suggests that Viscon-treated fuel introduced into the soil environment is likely to biodegrade in a manner similar to conventional diesel fuel.

Rates of flow (saturated hydraulic conductivity) of diesel fuel and Viscon-treated diesel fuel were measured in the lab using a sandy loam soil at two moisture contents (3% and 15%) packed in 5-cm diameter permeameters to a depth of 20 cm. Four replicate columns were used with each moisture content and with each fuel, and flow rates were measured using a constant head arrangement. The mean computed hydraulic conductivities for the two fuels were compared by a t-test, and found not to be statistically different at $p=0.05$ for either moisture condition, although Viscon-treated fuel flowed about 30% slower than untreated diesel. Our conclusion is that the Viscon additive would not have a practical effect on fuel migration in unsaturated field soils, and would therefore be unlikely to affect remediation strategies used to mitigate the environmental impact of spills or leakage of Viscon-treated diesel fuels. .

Paired comparison for the single hydrocarbons measured for diesel and viscon treated diesel
12/20/2010

Untreated Diesel Hydrocarbons

Analysis date	Dodecane	Tridecane	Tetradecan	Pentadecan	Hexadecan	Heptadecar	Octadecane	Nonadecan	**Eicosane**
3/26/2010	102.7	92.7	645.1	448.4	124.5	223.8	109.5	49.2	73.6
4/16/2010	100.9	113.2	414.8	380.1	143.9	274.4	130.4	281.0	36.0
5/6/2010	208.1	156.2	758.0	569.5	179.5	256.6	139.3	68.4	88.1
5/27/2010	133.4	105.8	491.6	110.8	86.5	145.6	76.6	24.6	29.4
6/16/2010	86.7	87.5	127.1	80.3	100.1	83.5	69.0	23.9	26.7

Viscon Treated Diesel Hydrocarbons

	Dodecane	**Tridecane**	**Tetrade ca**	**Pentadeca**	**Hexadecan**	**Heptadeca**	**Octadecan**	**Nonadecar**	**Eicosane**
3/26/2010	153.1	148.7	522.8	487.5	179.2	219.7	128.4	161.8	82.0
4/16/2010	214.2	220.9	230.0	161.5	353.2	205.8	200.2	180.0	38.4
5/6/2010	206.5	154.7	796.5	585.7	180.0	255.2	145.3	64.0	89.8
5/27/2010	137.1	107.7	512.8	86.0	83.5	146.2	77.7	12.6	32.3
6/16/2010	5.3	4.5	17.3	11.1	4.4	9.9	4.0	9.8	2.7

Dodecane:
t-Test: Paired Two Sample for Means

	Diesel	*V.T.Diesel*
Mean	126.3629	143.2539
Variance	2380.487	7048.395
Observations	5	5
Pearson Corre	0.522606	

Tridecane
t-Test: Paired Two Sample for Means

	Diesel	*V.T.Diesel*
Mean	111.0937	127.314
Variance	740.9159	6358.403
Observatio	5	5
Pearson Co	0.465781	

Tetradecane
t-Test: Paired Two Sam

	Diesel
Mean	487.3178
Variance	58288.4
Observatio	5
Pearson Co	0.958462

Appendix Table 1. Concentrations and T-tests for individual hydrocarbons in degradation experiments.

NB: Please double click on part of the table to see all the data.

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APPENDIX H

Multimedia Working Group Comments on Biodegradation and Environmental Fate Testing Report

MMWG Comments on:

First Submittal: 12/01/10, 12/13/10, 12/16/10
Final Submittal: 01/07/11, 01/18/11

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MMWG Comments on Viscon Multimedia Evaluation Report Received 11/18/10

Final Report and Memo Received – 11/18/10
Sent to MMWG on 11/18/10 – Internal Meetings, Comment Period 11/30/10 – 12/07/10

ARB COMMENTS

ARB – 1: For the analyses of the results obtained from the testing, please provide the raw data with the report.

ARB – 2: The UGA final report, entitled “Effect of Fuel Additive on the Environmental Fate of Diesel Fuel,” does not include information on potential impacts Viscon treated diesel may have on soil cleanup methods.

OEHHA COMMENTS

OEHHA – 1: While one of the tasks of the study (and knowledge gap of interest to MMWG) is "the potential soil cleanup impacts of Viscon-treated diesel" (p.3), which consists of "physical, chemical, and microbiological methods" (p.4) the report does not seem to provide analysis or conclusions clarifying this issue.

OEHHA – 2: It is difficult to evaluate the adequacy of the performed experiments to the objectives of the study since (according to my knowledge) no strict experimental design rules for such experiments are widely recognized or recommended. For example, why the soil moisture was selected at 3% and 15% (p.20).

OEHHA – 3: The statistical treatment of the impact on individual hydrocarbons is confusing. Namely the text on p. 14 "Assessment of the difference between the results of tables 6 and 7 was done by comparing the mean values reported in the right hand column in each table using the paired t-test of statistical analysis" is not what was done. In fact, the average of the individual component averages for CARB-diesel was compared to the average of the individual averages of Viscon-treated diesel. If the average of each individual diesel component (CARB) is compared to the Viscon-treated one statistically, the results may be different. Accordingly, the raw data may be studied further, if this is of interest to the MMWG.

OEHHA – 4: Editorial: p. 15 pages 15 and 17, and 16 and 18 should probably read 16 and 18, and 17 and 19;

OEHHA – 5: p. 20 VISON (in title) should read VISCON

OEHHA – 6: p. 22 "Flow rates did not stabilize until about (omega?) h after..."

Department of Toxic Substances Control

Maziar Movassaghi,
Acting Director
8800 Cal Center Drive
Sacramento, California 95826-3200

Linda S. Adams
Secretary for
Environmental Protection

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Li Tang, Ph.D, PE
Hazardous Substances Engineer
Multimedia Work Group
Pollution Prevention Program

FROM: Yun Zhang, PG
Engineering Geologist, Geological Services Unit
Office of Geology
Brownfields and Environmental Restoration Program

CONCUR: Dot Lofstrom, PG
Chief, Geological Services Unit
Office of Geology
Brownfields and Environmental Restoration Program

DATE: December 14, 2010

SUBJECT: VISCON FINAL REPORT, VISCON CALIFORNIA, LLC, BAKERSFIELD, CALIFORNIA

PROJECT CODE: 22110, GSU #: 910009

DOCUMENT REVIEWED

Effect of Fuel Additive Viscon on the Environmental Fate of Fuel Diesel, Viscon California, LLC, 3121 Standard Street, Bakersfield, California (Viscon Final Report). Prepared by Department of Crop and Soil Sciences, University of Georgia, Athens, Georgia, and dated November 2010.

INTRODUCTION

Per your request, the Geological Services Unit (GSU) of the California Department of Toxic Substances Control (DTSC) has reviewed the above document and has the following comments and recommendations. If you have any questions or comments regarding this memorandum, please contact Yun Zhang at (916) 255-3700 or yzhang@dtsc.ca.gov.

BACKGROUND AND REPORT SUMMARY

Viscon is an additive for diesel fuel which is being proposed by Viscon California as a strategy for reducing PM and NOx emissions for diesel engines. The active component of viscon is an ultra high molecular weight polyisobutylene (PIB) polymer. Viscon is used at less than 5 parts per million (ppm) to the end use CARB diesel. Prior to agency approval for marketing of Viscon Diesel, the California Environmental Protection Agency Multimedia Work Group requested Viscon California to address the knowledge gaps pertaining to fate, transport, biodegradation, and potential soil cleanup impacts of viscon-treated diesel compared to regular diesel fuel when a spill occurs.

The Viscon Final Report was prepared to summarize the laboratory testing results investigating the effect of fuel additive viscon on the environmental fate of regular fuel diesel. The goals of the laboratory testing include 1) filling the data gaps identified by the Multimedia Work Group pertaining to the fate, transport, and biodegradation of the Viscon diesel fuel in comparison to regular diesel fuel; and 2) discussing their potential impacts to the soil cleanup when a spill occurs.

GENERAL COMMENTS

Based on the review of the Viscon Final Report, it appears that the report contains a partial, and in some cases, inaccurate understanding of saturated and unsaturated flow concepts and the hydrogeologic variables (e.g. porosity versus permeability) which control flow. The report also contains mis-numbered figures and incomplete tables. In addition, the report does not discuss the potential impacts of Viscon diesel fuel to the soil cleanup actions when a spill occurs. Accordingly, the report should be revised and reviewed by a licensed professional geologist or certified hydrogeologist before submitting to the agency for review.

SPECIFIC COMMENTS

The GSU has the following specific comments that should be addressed in the final report:

1. As commented before, DTSC requested Viscon California to conduct research or perform laboratory tests to identify and compare the physical parameters that are associated with fate and transport properties of Viscon diesel and regular diesel fuel. These parameters include, but not limited to, viscosity, density, solubility in water, etc. These parameters should be tested to differentiate or characterize the two diesel fuels used in the laboratory tests and to help understand their fate and transport behaviors in the environment. Please conduct the testing and/or provide the results of this testing, if already performed, in the next version of the report.

2. For the soil columns packed for the flow test, the report should briefly describe how the porosity of each soil column is defined and derived at 0.45 for all moist (15% water content) soil columns and 0.5 for all dry (3% water content) soil columns.

3. The discussion of K_{sat} values and flow rates in the Results and Discussion Section on Page 22 is confusing and appears to be inaccurate. K_{sat} is calculated by using Darcy's Law under saturated flow for both diesel fuel columns. The relatively uniform values of K_{sat} calculated for both diesel fuel columns indicate that the porous media compacted in columns are relatively homogeneous. While K_{unsat} (hydraulic conductivity under unsaturated flow conditions) is related to water content, K_{sat} is not because the columns are saturated and the soil pores are filled up with diesel fuel (assuming the residual water is minimal when the columns are saturated and steady state flow is achieved). The K_{sat} values for initial dry and moist soil columns should not differ significantly for the same fluid in homogeneous media (soil columns) under saturated flow conditions. The definition of K_{sat} below is for your reference.

   $Ksat = k_0*(\rho g)/\mu$; where k_0 is intrinsic permeability ($k_0 = c*d^2$), c is constant, d is the diameter of pores in the soil column, ρ is fluid density, g is gravitational constant, and μ is fluid viscosity.

4. In the Results and Discussion Section on Page 22, the explanation of flow rate differences for diesel fuel in dry and moist soils is confusing and appears inaccurate. The flow velocity in saturated soil columns is not defined by bulk density and porosity (as stated in the report). Rather, the flow velocity is defined by hydraulic conductivity, hydraulic gradient and inter-connectivity of voids space within the columns (effective porosity). This is why flow in clayey soils is slow (high porosity, low hydraulic conductivity and pore interconnectivity), but flow in sandy and gravel soils is fast (low porosity, high hydraulic conductivity and pore interconnectivity).

Data Analysis

1. The t-test is to compare the difference of the means of two independently sampled and normally distributed data sets. It is not clear from the report if the preconditions required for the t-test were met. Data should be checked for satisfying preconditions or assumptions of the t-test before conducting the analysis. T-test assumes that data are independently collected and normally distributed for each data set. If these conditions are assumed but not checked due to limited number of samples, the report should explicitly state so. However, the conditions are not even mentioned in the report. Data analysis ignoring the assumptions may provide erroneous results.

2. To allow the reader to interpret the results properly, the statistical data analysis should be revised to address the following issues:

   a. Table 5 should be revised to define the last two columns as Viscon Diesel and Diesel, respectively, not the two numbers;

   b. In Tables 9 and 10, values of some parameters are incorrect and require revision. For example, "Coefficient of Variance" (CV) for checking of outliers is missing a percent (%) sign. "Confidence Interval" (CI) is incorrect. "t-probability" is not defined, and the values do not appear to be correct.

   c. The tables should be reorganized in a logical manner (for example, showing what is calculated first and what is calculated next).

3. In last two sentences of the Conclusions (Section VII), the explanation of the statistical analysis and results is subjective and potentially speculative. The laboratory tests indicate that the mean K_{sat} is ~30% lower for Viscon diesel fuel than regular diesel fuel, which is significant. However, the report states that this result is not significant based on the t-test. It is worthwhile to discuss which result better represents the predicted transport behaviors of the two diesel fuels in the porous medium. The final report appears to overreach the data analysis and conclusions to prove there is no significant difference in each fate and transport parameter of the two diesel fuels, especially for the transport. In fact, when a spill occurs, a slower migration of Viscon diesel may allow more time for cleanup actions than a faster migration of the regular diesel before they reach a groundwater body. The GSU would like to emphasize that it is acceptable for the results of the analysis to have differences, which appears to be the case according to the lab test data provided to date. The differences on transport behaviors for the two diesel fuels are unlikely to have negative impacts on soil cleanup actions when a spill occurs.

4. The Viscon Final Report does not include sections to discuss the impacts of Viscon diesel fuel, in comparison to regular diesel fuel, to environmental cleanup when a spill occurs. Such discussions should be included in the final report in accordance with the agreed goals.

State Water Resources Control Board

Division of Water Quality

Linda S. Adams
Secretary for Environmental Protection

1001 I Street, Sacramento, California 95814♦ (916) 341-5371
Mailing Address: P.O. Box 2231, Sacramento, California 95812
FAX (916) 341-5808 ♦ Internet Address: http://www.waterboards.ca.gov

Arnold Schwarzenegger
Governor

TO: Aubrey Sideco
FROM: Robert Hodam
DATE: December 1, 2010

RE: EFFECT of FUEL ADDITIVE VISCON on the ENVIRONMENTAL FATE of DIESEL FUEL: Final Comments

General Comment: the Water Board staff have no additional concerns as a result of this report. The fate and transport of CARB diesel contaning 5ppm PIB is not appreciably different than CARB diesel without PIB.

Question 1: Page 3 refers to "UHMWPIB … used as a method of controling releases of diesel fuel, approved for use in California". I think this refers to the use of PIB to help control "spills" from oil tankers in marine environments rather than "releases" from UST into groundwater. This is only a sematic difference, but if in fact VISCON means "releaes" from UST, then a reference to those data should be included.

Question 2: Page 13 reports that diesel with PIB flowed slightly slower than diesel without PIB over a period of less than an hour; this raises the hypothetical question as to whether the flow rate under constant head would continue to slow down if the timeframe were hours or days – enough time for the PIB to begin to fill soil pore spaces? If PIB slows the rate of release from a UST that may be a benefit to UST leak prevention and soil cleanup efforts of the Water Board.

<u>VISCON is NOT asked to answer that question as part of the nearly complete current verification process</u>. However, it may be a consideration for future product development by VISCON under a new verification application.

Robert Hodam
Alternative Fuels Lead
State Water Resources Control Board
rhodam@waterboards.ca.gov

MMWG Comments on Viscon Multimedia Evaluation Final Report dated Jan 3, 2011

Final Report and Memo Received – 11/18/10
Sent to MMWG on 11/18/10 – Internal Meetings, Comment Period 11/30/10 – 12/07/10
Internal MMWG Meeting to Discuss Comments/Concerns – 12/13/10
Sent Draft Comments to Viscon CA – 12/13/10
Conference Call with Viscon CA and UGA to Discuss MMWG Comments – 12/14/10
Revised Final Report and Test Data Received – 01/04/11
Sent to MMWG on 01/04/11

ARB COMMENTS

ARB – 1: The UGA final report, entitled "Effect of Fuel Additive on the Environmental Fate of Diesel Fuel," was revised as follows:

> Minor edits were made and some grammatical errors were corrected.
>
> The tables were corrected with proper titles.
>
> Some sections remain incorrectly numbered in the report. Section numbers are not consistent with the table of contents.

Report lacks substantial information to address MMWG comments.

ARB – 2: Some of the test data were submitted with the revised final report. The spreadsheets did not include all of the actual results, raw data, and calculations.

The results from the environmental transport study (column tests) were not provided. The spreadsheets contained the values and not the formulas used to calculate the values.

The graph illustrating the flow rate results from the column tests were provided for the moist soil samples (15% moisture content) but not the dry soil samples (3% moisture). A similar graph for dry soils would allow further comparative analysis of both the moist and dry soils. According to the results, dry soil columns tests reached a steady state very rapidly but for the moist soil samples, flow rates did not stabilize until about 30 minutes after initiation. Since there are differences in the flow rates of the two different types of soil, graphs similar to Figure 10 for both dry and moist soil results would be beneficial to include in the report.

The statistical analysis and the specific assumptions and parameters used in the analysis were not clarified in the report.

The biodegradation tests did not follow the test protocol approved by the MMWG. From previous internal meetings with Viscon CA and UGA, the MMWG recommended UGA to identify and justify the proposed changes to the September 2009 test protocol. Were there any concerns with compositing all replicates into one sample? Would it negate an outlier that could provide additional information for analysis? In addition, there would be the possibility of one contaminated sample afftecting the other samples when combined.

The total petroleum hydrocarbons (TPHs) test results and statistical analysis data from the biodegradation tests, provided in table 4 and 5 of the report and TPH calculator spreadsheet, are incorrect. The graph shows five data points for the comparison but the Anova analysis calculated only four. It seems the March 23, 2010 data point is not included in the analysis.

The conclusion seems to be inconsistent with the test results and data analysis. Column test results show that “the Viscon-treated fuel K_{sat} values were about 30% lower than the regular diesel fuel (p23).” The conclusion that “the Viscon additive would not have a practical effect on fuel migration in unsaturated field soils” needs further clarification. Expand upon what is the practical effect and what benefits or consequences would result if there was a statistical difference.

ARB – 3: The report was revised to include more information on the potential impacts the additive may have on soil cleanup methods. However, only a few general statements were made throughout the report, as follows:

- I. General Introduction (p4): “Of equal importance is the flow capacity of the soil since during a remediation process, *flow rate of spilled diesel through soils has an important impact on remediation.”*

- I. Impact of Viscon on Diesel Biodegradation, 1. Introduction (p4): *“The inclusion of Viscon at the 5 ppm range should not be expected in any way to impact the harsh physicochemical remedation techniques of diesel. Due to the highly sensitive nature of microbrial growth and liability of remediation techniques derived there from, it is necessary to study the impact of low concentration of chemical additives on its microbiological remediation.“*

- VII. Flow of Viscon-Treated Diesel Fuel Through Soil Columns (p20): *“Flow rate is an important consideration in remediation of fuel spills, and it is desirable that fuel additives do not increase the rate of flow.”*

- VII. Conclusion (p25): *“This result suggests that Viscon-treated fuel introduced into the soil environment is likely to biodegrade in a manner similar to conventional diesel fuel.*

  …

  Our conclusion is that the Viscon additive would not have a practical effect on fuel migration in unsaturated field soils, and would therefore be unlikely to affect remediation strategies used to migrate the environmental impact of spills or leakage of Viscon-treated diesel fuels.”

In addition to these general statements added in the report, a complete and separate analysis of potential impacts should be studied and provided as a separate report or separate section in the report.

The actual analysis of the test data and the scientific explanation of potential impacts based on the test results must be further developed in order to justify the conclusions stated in the report.

Linda S. Adams
Acting Secretary for
Environmental Protection

Department of Toxic Substances Control

Maziar Movassaghi
Acting Director
1001 "I" Street
P.O. Box 806
Sacramento, California 95812-0806

Edmund G. Brown Jr.
Governor

MEMORANDUM

TO: Aubrey Sideco
Air Resources Engineer
Air Resources Board

FROM: Li Tang, Ph.D., P.E.
Toxic Substances Engineer
Multimedia Products Section
Department of Toxic Substances Control

Yun Zhang, PG.
Engineering Geologist, Geological Services Unit
Office of Geology
Department of Toxic Substances Control

VIA: Andre Algazi, Chief
Consumer Products Section
Multimedia Products Section
Department of Toxic Substances Control

SUBJECT: DTSC Comments on Revised Viscon Final Report Dated January 3, 2011

DATE: January 18, 2011

DTSC has reviewed the revised Final Report "Effect of Fuel Additive Viscon on the Environmental Fate of Diesel Fuel," dated January 3, 2011. The report, prepared by the University of Georgia's Department of Crop and Soil Sciences on behalf of Viscon California, LLC, updates the November 2010 version to address concerns raised by the California Environmental Protection Agency's (Cal/EPA) Multimedia Working Group. DTSC's evaluation of the report focuses on its analysis of the effects of the additive on the persistence and migration of diesel fuel in soil in the event of a spill. While the January 3, 2011 revision is an improvement on the November 2010 version, DTSC continues to have questions and concerns about the report, which are enumerated below.

General observations

1. Sections are still mis-numbered, and titles are not consistent with the content in some sections.
2. Font sizes are not consistent in some tables (for example, Tables 6 and 7).

Specific issues and questions

1. The report does not discuss the impact of Viscon on soil remediation when a spill occurs. The University of Georgia indicated during our most recent meeting with them, that they were not specialists in soil remediation technologies; the authors' lack of expertise does not justify forgoing even a cursory evaluation of soil remediation based on the findings of their laboratory tests.
2. The assumptions and conditions for the authors' t-test analyses are not stated. Nor do the authors provide their rationale for selecting a t-test over other statistical methods. It is unclear why they use paired comparison analysis for the biodegradation test data (Table 5), but not for the flow test data (Tables 9 and 10).
3. Laboratory testing data for flow rates are not included appropriately in tables. For example, the data for flow rate (measured) and Ksat (calculated) for each soil column should have been listed in tables for both 3 percent and 15 percent soil moisture contents. The report also does not include raw data for the transport tests (the only raw data provided are for biodegradation testing).
4. Statements about the viscosity of CARB diesel in the current report differ from those in earlier reports; the report fails to note or explain the discrepancy:
   - Page 6 of Viscon's Tier II Report, dated April 28, 2009 cites "2.33 Centipoise (cP) at 1,800 reciprocal seconds (D(1/s) for CARB diesel...";
   - In this final report, page 21: "Fuel materials (either CA-approved diesel fuel or Viscon-amended diesel, supplied by Viscon California LLC) were reported to have equal specific gravities (0.83) and viscosities (1.80 cP) by the supplier."
5. In Figure 3 (page 12); the values on the x-axis (Date) do not align with the data points and are not consistent with the dates shown in Table 4 (page 11). Appropriate adjustment of the scales in Figure 3 would be needed to show each data point clearly.
6. The titles for Tables 9 and 10 are unclear - are the data for K_{sat}?

7. A figure showing flow rate change for 3 percent moisture content soil columns should have been included in the report, similar to Figure 10 (for 15 percent moisture content).

8. Page 23 of the report asserts that "... in a practical field situation ... [the lower K_{sat} values for Viscon-treated fuel] would not be likely to have a major impact on fuel migration rates through soils." The conclusion (last sentence on Page 25) makes a similar statement. However, the report does not elaborate why the measured 30 percent difference in migration rate between these two diesels is not important. What do the authors mean by "a practical effect"? DTSC feels the results could have been better interpreted in terms of potential impacts to soil cleanup when a spill occurs.

If you have any questions, please contact Dr. Li Tang at (916)322-2505 or at ltang@dtsc.ca.gov.

APPENDIX I

Request for External Peer Review of the Multimedia Evaluation of Viscon Diesel Fuel Additive

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Linda S. Adams
Secretary for Environmental Protection

Air Resources Board

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Arnold Schwarzenegger
Governor

TO: Gerald W. Bowes, Ph.D.
Manager, Cal/EPA Scientific Peer Review Program

FROM: Dean C. Simeroth
Chief, Criteria Pollutants Branch

DATE: November 4, 2009

SUBJECT: REQUEST FOR EXTERNAL PEER REVIEW OF THE MULTIMEDIA EVALUATION OF VISCON DIESEL FUEL ADDITIVE

The California Air Resources Board (ARB) staff requests, by transmittal of this memorandum, that you initiate the process to identify and assign reviewers to provide external scientific peer review of a multimedia evaluation per the requirements of Health and Safety Code (H&S) section 57004.

Viscon is a proprietary diesel fuel additive being verified as a Level 1 diesel emission control strategy under the Diesel Emission Control Strategy Verification Procedure ("Verification Procedure") pursuant to Title 13, California Code of Regulations (CCR), section 2700 et seq. The Verification Procedure requires a multimedia evaluation to be conducted, peer reviewed, and submitted to the California Environmental Policy Council (CEPC) pursuant to H&S section 43830.8. The CEPC, as established by Public Resources Code section 71017, will determine whether the use of Viscon will cause a significant adverse impact on human health or the environment, including air, water and soil.

The California Environmental Protection Agency (CalEPA) formed the Multimedia Working Group (MMWG) to oversee the multimedia evaluation process and make recommendations to the CEPC regarding the acceptability of new fuel formulations. The MMWG, whose members include staff from the Air Resources Board (ARB), State Water Resources Control Board (SWRCB), Office of Environmental Health Hazard and Assessment Office (OEHHA), and the Department of Toxics Substances Control (DTSC), is submitting the multimedia evaluation staff report for external peer review.

Pursuant to the Verification Procedure, the multimedia evaluation must be completed before Viscon can be verified as a viable diesel emission control strategy. Therefore, staff requests that the review be **completed and comments from reviewer(s) received by January 15, 2010.** The staff report and supporting documentation, including the Viscon reports, will be ready for review by December 1, 2009.

We recommend that you solicit at least four reviewers with expertise in environmental and multimedia impacts analysis, including: (1) air quality; (2) surface and ground water quality, (3) public health, and (4) soil impacts from hazardous waste.

Please note that there is one other fuel additive (Lubrizol PuriNOx) verified and approved for use in California; information related to this additive can be found at: http://www.epa.gov/OTAQ/retrofit/techlist-lubrizol.htm.

There are three attachments to this memorandum:

1. Summary of the Viscon Multimedia Evaluation
2. Descriptions of the Scientific Issues to be Addressed by Peer Reviewers
3. Individuals Involved in the Multimedia Evaluation Process

We request that the process to find peer reviewers begin immediately, and that comments from reviewers be returned to me by January 15, 2010, or by a date that is mutually agreed upon.

If you should have further questions regarding this request, please feel free to contact Aubrey Sideco at (916) 324-3334 or via email at asideco@arb.ca.gov. Thank you for your assistance.

Attachments

cc: Aubrey Sideco
Air Resources Engineer
Industrial Section

Attachment 1

Summary of the Viscon Multimedia Evaluation

I. Background

Viscon California, LLC applied for verification of its proprietary fuel additive, Viscon, under the Diesel Emission Control Strategy Verification Procedure ("Verification Procedure") pursuant to Title 13, California Code of Regulations (CCR), section 2700 to 2710. Section 2710(f) requires a multimedia evaluation to be conducted for all fuel additives. The applicant, Viscon California, LLC, and the Multimedia Working Group (MMWG) conducted a multimedia evaluation of Viscon pursuant to Health and Safety Code (H&S) section 43830.8 and the *Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations.*

According to the Verification Procedure, Viscon may not verified unless a multimedia evaluation has been conducted and the California Environmental Policy Council (CEPC), as established by Public Resources Code section 71017, has determined that the there will not be a significant adverse impact on public health or the environment, including air, water, and soil, that may result from the production, use, or disposal of the fuel additive.

I. Viscon Multimedia Evaluation

With the MMWG, Viscon California, LLC conducted a multimedia evaluation of Viscon fuel additive. Based on the results of the evaluation and the information contained in the Viscon reports, the MWWG makes the overall conclusion that Viscon will not cause significant impacts. As determined by members of the MMWG, the effects of the additive, either alone or in additized diesel fuel, are expected to be less than or equal to CARB diesel itself. Tests on the effects on air quality, human health, and soil and water quality are summarized here.

Air Quality. Based on emissions testing, the MWWG concludes that the additive generally reduces air emissions from treated fuel. In tests of toxic emissions with pre-durability and post-durability tests, reductions from the baseline were found in the majority of carbonyls and in the majority of polycyclic aromatic hydrocarbons. A potential increase in volatile organic compounds was also found in the results of the testing.

Human Health. In exposure assessments, the MWWG found that there is no significant risk to human health expected to result from production, transportation, handling, storage or use of the Viscon additive in addition to the risk normally associated with the use of CARB diesel. There is a significant benefit to human health associated with the use of the Viscon additive to reduce harmful exhaust emissions from California's diesel engine inventory. Addition of Viscon to CARB diesel reduces harmful exhaust emissions when compared to exhaust emissions from untreated CARB diesel, with particulate matter emissions reduced an average of 25 percent.

Soil and Water Quality. Based on estimates of chemical properties of additized CARB diesel, the MWWG has determined that the Viscon additive poses no more risk than CARB diesel in potential release scenarios to soil or an aquatic ecosystem. In staff's evaluation, the MWWG found a potential for an increase in cohesiveness, which reduces the tendency of the fuel to disperse in water.

Although there were knowledge gaps indentified, the MMWG determined that, even with these knowledge gaps, the potential risks are minimal and acceptable, based on the expected limited use of Viscon and information contained in the staff report, Viscon reports, and supporting documents. According to the conditional approval set forth by the MMWG, the applicant is required to submit the following two documents within one year: (1) laboratory tests for biodegradability and fate and transport in soil and (2) a technical report illustrating Viscon's potential impact on different soil cleanup methods.

If peer reviewers determine that the conclusions and recommendations made by the MMWG are based upon sound scientific knowledge, methods, and practices, including the overall finding that Viscon, as conditioned in the multimedia evaluation, does not pose any significant adverse impact on public health or the environment, the MWWG proposes to submit the multimedia evaluation summary to the CEPC for approval of the Viscon additive.

III. Staff Report: Multimedia Evaluation of Viscon Fuel Additive

Pursuant to H&S section 43830.8, a written summary of the multimedia evaluation shall be prepared and submitted for external scientific peer review in accordance to H&S section 57004. The information upon which the staff report is based, including the Viscon reports, test protocol and design, test results, raw data and other supporting documentation, will be submitted with the main staff report.

The staff report is a summary of the multimedia evaluation and includes the conclusions and recommendations of the MMWG to the CEPC regarding the acceptability of the fuel additive for use in California. The staff report is based on the information and data gathered during the multimedia evaluation process, including the Viscon reports and raw data submitted by Viscon California, LLC. The Viscon reports include background information on the fuel additive, testing designs and protocols, publications, test results, and other supporting documentation.

Attachment 2

Descriptions of Scientific Issues to be Addressed by Peer Reviewers

The statute mandate for external scientific peer review (H&S section 57004) states that the reviewer's responsibility is to determine whether the scientific portion of a proposed rule is based upon "sound scientific knowledge, methods, and practices."

We request that you make this determination for each of the following issues that constitute the scientific basis of the staff report. An explanatory statement is provided for each issue to focus the review.

For those work products which are not proposed rules, as with the subject of this review, reviewers must measure the quality of the product with respect to the same exacting standard as if it was subject to H&S section 57004 requirements.

The staff report and data upon which the staff report is based will be provided in disk form and hard copies upon request.

1. Air Emissions Evaluation

Air Resources Board (ARB) staff conducted an emissions evaluation to assess the air quality impacts of the proposed Viscon fuel additive. The evaluation includes a summary of emissions results, including criteria pollutants, toxic air contaminants, and ozone precursors. Based on a relative comparison between diesel fuel complying with ARB requirements (CARB diesel) and CARB diesel with the Viscon additive, ARB staff concludes that the use of Viscon additive does not pose a significant adverse impact on public health or the environment from potential air quality impacts, relative to conventional California diesel fuel. The reviewers of the multimedia evaluation summary must assess the air emissions evaluation and ARB staff's conclusions and recommendations to the California Environmental Policy Council.

2. Water Evaluation

State Water Resources Control Board (SWRCB) staff completed an evaluation of the impacts on surface water and groundwater from the use of Viscon. The evaluation includes a summary of the SWRCB's considerations when evaluating new fuels and fuel additives. Based on the evaluation of Viscon, staff considered potential issues with material compatibility, biodegradability, fate and transport, aquatic toxicity, and impacts on soil clean up. Based on relatively non-toxic nature of the additive, its low dose rate, and the insolubility of the additive's active component, SWRCB staff concludes that the use of Viscon does not pose risks to water resources. The reviewers must assess SWRCB staff's conclusions and recommendations.

3. Public Health Evaluation

Office of Environmental Health Hazard and Assessment Office (OEHHA) staff evaluated potential human health impacts from the use of Viscon. The evaluation includes a summary, conclusions, and recommendations by OEHHA staff in regards to potential impacts to public health or the environment. The reviewers must assess the evaluation.

4. Soil and Hazardous Waste Evaluation

Department of Toxics Substances Control (DTSC) staff completed an evaluation of potential soil and hazardous waste impacts from the use of Viscon. The evaluation includes a summary, conclusions and recommendations by the DTSC staff. The reviewers must assess the evaluation.

5. The recommendations of the Multimedia Working Group to the California Environmental Policy Council (CEPC), including the overall finding, as conditioned in the multimedia evaluation, that Viscon does not pose any significant adverse impact on public health or the environment.

The proposed recommendation to the CEPC is to find that the use of Viscon additive does not pose any significant adverse impacts on public health or the environment relative to conventional CARB diesel.

<u>The Big Picture</u>

Reviewers are not limited to addressing only the specific issues presented above, and are asked to contemplate the broader perspective:

- **(a) In reading the staff report and supporting documentation, are there any additional scientific issues that are part of the scientific basis of the multimedia evaluation of the proposed fuel additive not described above? If so, please comment with respect to the statute language given above.**

- **(b) Taken as a whole, is the scientific portion of the multimedia evaluation based upon sound scientific knowledge, methods, and practices?**

Reviewers should also note that some proposed actions may rely significantly on professional judgment where available scientific data are not as extensive as desired to support the statute requirement for absolute scientific rigor. In these situations, the proposed course of action is favored over no action.

The preceding guidance will ensure that reviewers have an opportunity to comment on all aspects of the scientific basis of the multimedia evaluation of a proposed fuel additive. At the same time, reviewers also should recognize that

the Board has a legal obligation to consider and respond to all feedback on the scientific portions of the multimedia evaluation. Because of this obligation, reviewers are encouraged to focus feedback on the scientific issues that are relevant to the central regulatory elements being proposed.

Attachment 3

Individuals Involved in Multimedia Evaluation Process*

Viscon California, LLC	
Michael Porter	Viscon California, LLC
Patrick Porter	Viscon California, LLC
Preston Wahl	Viscon California, LLC
Consultants	
Sayed Hassan	University of Georgia
William Miller	University of Georgia
Rick Margolin	Innovo Energy Solutions Group, LLC
Daniel Emmett	Innovo Energy Solutions Group, LLC
Multimedia Working Group Members	
Aubrey Sideco	Air Resources Board
Robert Okamoto	Air Resources Board
Floyd Vergara	Air Resources Board
Dean Simeroth	Air Resources Board
Jim Guthrie	Air Resources Board
Linda Lee	Air Resources Board
Alexander Mitchell	Air Resources Board
Marcie Pullman	Air Resources Board
Rodney Hill	Air Resources Board
John Lee	Air Resources Board
Jim Peterson	Air Resources Board
Kirk Rosenkranz	Air Resources Board
Mark Schuy	Air Resources Board
Shawn Daley	Air Resources Board
Robert Hodam	State Water Resources Control Board
James Giannopoulos	State Water Resources Control Board
Li Tang	Department of Toxics Substances Control
Sonia Low	Department of Toxics Substances Control
Sherri Lehman	Department of Toxics Substances Control
Xiao Ying Zhou	Department of Toxics Substances Control
Page Painter	Office of Environmental Health Hazard Assessment
Bruce Winder	Office of Environmental Health Hazard Assessment
Hristo Hristov	Office of Environmental Health Hazard Assessment
Melanie Marty	Office of Environmental Health Hazard Assessment
Andy Salmon	Office of Environmental Health Hazard Assessment

* No person may serve as an external scientific peer reviewer for the scientific portion of the multimedia evaluation if that person participated in the development of the scientific basis or scientific portion of the multimedia evaluation.

APPENDIX J

External Scientific Peer Review Comments

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Review of Multimedia Evaluation of VISCON Diesel Fuel Additive

Prepared by
Professor Yoram Cohen
Chemical and Biomolecular Engineering Department
University of California, Los Angeles
Los Angeles, CA 90095

The Multimedia Evaluation of the Viscon Diesel Fuel Additive, performed by the Multimedia Working Group (MMWG) convened by the California Environmental Protection Agency, was reviewed to assess the scientific basis for the evaluation by the MMWG to the California Environmental Policy Council (CEPC). The review of the collection of evaluation documents [1-4] provided to the reviewer followed the guidelines provided in documents [5] and [6].

The VISCON Fuel Additive

Viscon is a diesel fuel additive consisting of solution of a 1% (by wt) high molecular weight polyisobutylene (PIB) dissolved in diesel fuel. This additive is added to diesel fuel such that the resulting concentration in the fuel mixture is about 5 ppm. An evaluation of the potential environmental and health impacts of Viscon was carried out by a Multimedia Working Group (MMWG) to evaluate the following:

a. Impact of Viscon on emissions of air pollutants including air toxics, particulate matter, greenhouse gases and ozone-forming chemicals;
b. Potential contamination of soil, groundwater and surface water associated with the production, storage, use and disposal of Viscon;
c. Environmental implications of the disposal of Viscon and/or Viscon containing waste materials
d. Health impacts associated with the production, storage, use and disposal of Viscon

Overall, the evaluation as presented by the MMWG followed basic scientific understanding. Specific review comments pertaining to the MMWG evaluation of Viscon [1] addresses the following issues: (1) the physicochemical properties of Viscon and its active ingredient (PIB) that are relevant to assessing the transport and fate of the Viscon additive, (2) Volatilization of Viscon and Viscon treated diesel, (3) Viscon transport in soil and water, (4) Air quality assessment of Viscon treated diesel fuel, and (5) health risk assessment.

1. Physicochemical Properties of VISCON and PIB

Viscon contains polyisobutylene (PIB) as its active ingredient. PIB is a synthetic rubber having the chemical formula of $(C_4H_8)_n$. It is a homopolymer of 2-methyl-1-propene. The Viscon formulation uses PIB of average molecular weight of ~$1x10^7$ ([2], Section II-B). A brief discussion of the basic physicochemical properties of PIB which are relevant to the environmental transport and fate of Viscon is provided below.

- **Aqueous solubility**. PIB is a non-volatile water insoluble synthetic rubber.

- **Vapor pressure**. The addition of PIB to diesel is likely to reduce the vapor pressure of some or most of the volatile components in the fuel mixture. Vapor pressure depression is a well known effect of when a soluble non-volatile is added to a liquid solution [7, 8]. Specific information regarding the vapor pressure depression upon the addition of PIB was not provided in the Viscon evaluation documents.

- **Viscosity.** In the Viscon formulation PIB is dissolved in CARB diesel at concentration at 1% by wt. The resulting fuel mixture is then added to diesel fuel in which PIB is then at a concentration of less than ~5 ppm. High molecular weight (MW) PIB, as most high MW polymers, when dissolved in a suitable solvent, increases the shear viscosity of the solution and also imparts viscoelastic behavior to the resulting solution [9-15]. One would expect that the viscosity of the resulting diesel fuel mixture (i.e., containing Viscon) would increase relative to CARB diesel. A Viscon viscosity of 0.5797 (g/cm·s) relative to 0.0233 (g/cm·s) for CARB diesel was reported at shear rate of 1,800 s^{-1} ([2, 3], Section III-D.2II). A Viscon viscosity of ~0.44-0.48 (g/cm·s) was reported[1] for shear rate of 250 s^{-1}. The above behavior is inconsistent with the expected shear-thinning behavior of polymer solutions. Extensional viscosity (obtained from oscillatory measurements) was provided for an alternate polymer but not for the specific PIB used in the Viscon additive. The assessment of the viscosity behavior, as reported in the Tier I [2] and Tier II [3] reports, is imprecise and it is worth noting the following:

    - Shear viscosity of PIB solutions would be expected to decrease with increasing shear. Extensional viscosity could increase with the extensional deformation rate (or elongational strain rate). Such effects are not temporary, but are sustained as long as the shear rate or elongational strain rate are maintained.

    - The zero-shear viscosity or viscosity at low shear (significantly less than the 1,800 s^{-1} cited in the Tier I Report [2]) is the viscosity relevant to evaluating the transport of Viscon or Viscon containing CARB diesel in soil and water.

    - Viscosity information for Viscon or diesel fuel containing Viscon was not available in the documents provided to the reviewer. Data on viscosity and viscoelastic behavior were provided for a product claimed to be similar (Elastosol; Attachments 9 and 10, [2]); it is unclear if the two products are of the same molecular weight.

- **Reactivity**. The degradation of PIB under environmental conditions is slow (years). It is a polymer that is not readily oxidized or biodegraded. However, specific degradation half-lives (under typical environmental conditions) for the high MW PIB used in Viscon have not been provided.

2. Volatilization

The addition of a high molecular weight additive to a solvent will decrease the vapor pressure of the solvent. For this reason, fugitive emissions from Viscon storage facilities and during transportation and use are likely to be lower than for diesel when both products are handled in precisely the same way. Also, due to the reduction of vapor pressure, it is likely that the rate of volatilization of a portion of the light diesel constituents will be reduced relative to untreated diesel.

[1] Note: 1 mPa·s = 1cP = 0.01 g/cm·s

3. Transport in Soil and Water

Quantitative information regarding soil infiltration and sorption of PIB (from Viscon or Viscon containing diesel fuel) was not provided. The viscosity of Viscon and diesel fuel containing the Viscon additive formulation will reduce the mobility of these fluid mixtures. Therefore, a specific evaluation of the efficacy soil cleaning methods may be warranted to assess the effect of viscosity as well as viscoelasticity. Another issue that requires attention is the sorption of PIB onto soil particles and the effect of soil organic carbon on such partitioning.

The spreading of Viscon or Viscon containing diesel on water (e.g., as a result of a spill) is likely to be less than for diesel given the higher shear viscosity and viscoelasticity of these formulations. It is possible that spreading of an oil slick may be also impacted by a change in the surface tension due to the presence of PIB; however, surface tension information was not provided regarding the surface tension of Viscon or CARB diesel containing Viscon.

4. Exhaust Emissions and Implications for Human Health Risks

The MMWG report [1] provided detailed analysis of criteria pollutants emissions from Viscon containing diesel fuel reported. Emission increased for nitric oxide (2.5%), while decreased emissions were reported for carbon dioxide (1.3%) and particulate matter (25%). According to the ARB about 70% of toxic risks from identified toxic air contaminants are associated with diesel particulate matter (PM). Therefore, it was reasonably reasoned that the 25% reduction in PM emissions achieved with the use of Viscon could lead to significant reduction in health risks associated with diesel related PM emissions.

Analysis of health risks associated with emissions of air toxics was provided by the MMWG (Attachment D) for acetaldehyde, formaldehyde and benzene. It was concluded that the upper-bound lifetime risk increase attributed to emission from diesel fuel containing Viscon would be of the order of 10^{-9} - 10^{-10}. It is noted that the average emission of 1,3,-butadiene, associated with Viscon containing diesel fuel, was reported to be 1,640% above the baseline [[1]; Table 4]. However, the MMWG did not consider health impacts associated with 1, 3-butadiene; it is unclear 1,3,-butadiene is being assessed by the MMWG as a non-toxic air pollutant.

References

[1] California Environmental Protection Agency, Multimedia Evaluation of Viscon, January 14, 2010, *prepared by ARB, OEHHA, SWRCB and DTSC*.

[2] Viscon 'Multi Media Evaluation (Tier I), prepared by Las Palmas Oil and Dehydration Company, 3121 Standard Street Bakersfield, California 93308, October 24, 2008. *Document prepared for Mr. Dean Bloudoff, California Air Resources Board Research Division, 1001 I Street, Sacramento, CA 95814.*

[3] Viscon Multi Media Evaluation (Tier II), prepared by Las Palmas Oil and Dehydration Company, 3121 Standard Street, Bakersfield, California 93308. *Prepared for Aubrey Sideco, California Air Resources Board, Stationary Source Division, 1001 I Street, Sacramento, CA 95814, March 16,* 2009.

[4] Viscon Multimedia Evaluation (Tier III) Summary, prepared by Viscon California, LLC, 3121 Standard Street, Bakersfield, California 93308. *Document prepared for Aubrey Sideco, California Air Resources Board, Stationary Source Division, 1001 I Street, Sacramento, CA 95814.*

[5] G.W. Bowes, Supplement to Cal/EPA External Scientific Peer Review Guidelines - "Exhibit F" in Cal/EPA Interagency Agreement with University of California, January 7, 2009.
[6] Dean C. Simeroth, Request for External Peer Review of the Multimedia Evaluation of Viscon Diesel Fuel Additive, Air Resources Board, Criteria Pollutants Branch, November 4, 2009.
[7] B. Bersted, Molecular weight determination of high polymers by means of vapor pressure osmometry and the solute dependence of the constant of calibration, Journal of Applied Polymer Science, 17 (1973) 1415.
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[9] J. Ferry, Viscoelastic properties of polymers. John Wiley & Sons Inc, 1980.
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[13] P. Rouse Jr and K. Sittel, Viscoelastic properties of dilute polymer solutions, Journal of Applied Physics, 24 (1953) 690.
[14] A. Sakanishi, Dynamic Viscoelastic Properties of Dilute Polyisobutylene Solutions, The Journal of Chemical Physics, 48 (1968) 3850.
[15] J. Van Nieuwkoop and M. Muller von Czernicki, Elongation and subsequent relaxation measurements on dilute polyisobutylene solutions, Journal of Non-Newtonian Fluid Mechanics, 67 (1996) 105.

Review of the Multimedia Evaluation of Viscon
Armistead Russell

Viscon, a proposed additive to diesel fuel in California, has undergone a series of tests and analyses of those tests, to assess the potential impacts of the use of Viscon in non-road applications. In their summary "Multimedia Evaluation of Viscon", the California Environmental Protection Agency (Cal-EPA) has assessed the data provided on the potential impacts of the use of Viscon in California. In general, the evaluation found that the use of Viscon does not pose a significant adverse threat to public health of the environment. This review of the CAL-EPA evaluation and the documentation provided, is primarily conducted based on the potential impacts on air quality in line with the Reviewer's expertise.

The data and analyses provided support, with some notable concerns still open, that the use of Viscon does not pose a threat to public health when used in diesel engines that do not have post-combustion controls such as oxidation catalysts. This conclusion is based upon the findings that particulate matter (PM) emissions appear to be reduced, and emissions of nitrogen oxides (NOx) and carbon monoxide (CO) are not significantly impacted. However, there are two very significant open concerns. First, the staff did not evaluate the potential impacts of the very significant increase in 1,3 butadiene reported in "Viscon Multi Media Evaluation (Tier III) Summary" prepared by Viscon California LLC. This summary finds a 1682% increase in 1,3 butadiene. The Staff Report on Health Impacts of Viscon Fuel (Dec. 2009) did not consider this potentially harmful compound. Given the composition of Viscon, it is not unexpected to see an increase in emissions of 1,3 butadiene.

A second concern is that only one engine was used in this testing. Different engines can respond differently to fuel changes, and in-use engines can respond differently than test engines, so the results found should only be viewed as supportive for a providing a potential reduction in PM. On the other hand, those results, along with other studies using other organic additives to diesel fuel at such low levels, that one should expect little significant increase in NOx or CO. Thus, the finding that using Viscon as an additive to diesel in off-road application likely poses little threat for increasing NOx or CO is quite reasonable. However, I would like to see more engines tested before being comfortable saying that a significant decrease would be found in diesel PM emissions from using Viscon as a fuel additive.

Given that a fraction of the diesel PM emissions is due to partial combustion of lubrication oil, it would have been of interest to see an analysis of what fraction of the diesel PM was being reduced, and the mechanism of reduction. While the major physical attribute that is discussed in the documents is its impact on viscosity under shear, this does not directly imply anything about its combustion characteristics, and if its use would decrease PM formation from lubricating oil partial combustion.

In the CARB "Assessment of Emissions of Viscon Diesel on Exhaust Emissions from Heavy-Duty Engines", they note that the increase in NOx was not statistically significant.

This brings up two issues. First, at what level is the increase not significant? Second, throughout the various evaluations, it would be useful to more completely show standard deviations (and adequately identify them as to what type, i.e., of the sample versus the mean). They further note that total HC increased by 6.2%. However, NMHC increased 54.3%. This would appear to be significant, and in need of greater consideration.

In Table 2 of “Assessment of Emissions of Viscon Diesel on Exhaust Emissions from Heavy-Duty Engines” they provide the covariances. This should be defined mathematically and a more complete discussion of its meaning would be useful. That table should also provide the standard deviations in the Pre and Post-durability tests. In Table 4 of that report, they do not note that there is a potential problem with the pre-durability measurements of 1,3 butadiene.

Given the above considerations, the Staff’s Conclusions (section III of the “Multimedia Evaluation of Viscon”), that the use of Viscon as an additive does not pose a significant threat to public health or the environment from potential air quality impacts should be qualified as such:

- Pending an assessment of the potential health effects of the increased 1,3 butadiene emissions, and
- That the use is limited to diesel engines that do not have post-combustion oxidation devices.

Further, it should be noted that there is a difference between the likelihood that it does not pose a potential adverse effect” and “that it likely will improve air quality”. Making the latter statement should be backed up further with experiments conducted on additional engines unless it can be shown that the engine used in these tests adequately represents the fleet of engines likely used in the intended application. Further, the bullets in the section on the Conclusion on Air Emissions Impact should consider that without toxicity testing of the PM emissions themselves, the reduction in health risk from a PM reduction may not be true if the per mass toxicity increases more so. Likewise, the third bullet should be removed, noting the potentially large increases in 1,3 butadiene, unless further analyses demonstrate the statement to be true. The fourth bullet likewise must account for the above issues.

The conclusion that the relatively non-toxic properties of PIB, along with the physical properties of the additive, support the conclusion that the water impacts are likely to be very similar to that posed by diesel, alone.

The Conclusion on Public Health Impact is true, noting that it uses the term “may reduce”. As noted above, further analysis is required to provide a more definitive statement.

The Conclusion on Soil and Hazardous Waste Impact appears well supported.

In regards to Recommendations, the statements are true if modified in accordance with the suggested changes to the Conclusion on Air Emission Impact and Public Health

Impact. Recommendation 3 should be more strongly brought forth in the reports as this important issue does not come through very strongly.

Except for the gaps identified above (need for an assessment of the potential impacts of the health effects of 1,3 butadiene and the desire to have more testing to make more definitive statements), the Multimedia Evaluation of Viscon does provide support for the determination that the use of Viscon as an additive for diesel fuel poses little increased threat to human and environmental health in the specified applications. The most immediate need is for staff to conduct an assessment of the potential impacts of the increased 1,3 butadiene emissions increases. Further testing, particularly using a different engine is needed to provide more support for a general conclusion that Viscon will reduce PM emissions. To provide adequate support for the statement in regards to that the PM reductions lead to a reduced health risk, toxicity testing of the diesel PM should be conducted.

Review:

Tier II and Tier III Multimedia Assessments of Viscon

Frank A.P.C. Gobas, Ph.D.

Simon Fraser University

February 2, 2010

Review Comments

The objective of this review is to provide a scientific evaluation of the Tier II and Tier III multi-media assessment of the product Viscon.

Viscon consists of a 1% solution of polyisobutylene (PIB) in CARB diesel. Since polyisobutylene is the active ingredient in the formulation, this evaluation will focus on polyisobutylene and its role in the application of Viscon.

The focus of the Tier II and III multi-media assessment has been on the effect of PIB on various key measures of air quality. Information is provided to substantiate the conclusions that the addition of PIB reduces particulate matter (PM) emissions by approximately 25%. In addition to a reduction in PM, the addition of PIB also reduces the production of lower molecular weight PAHs. Some of these substances are carcinogens. The reduction of PAHs may therefore lead to a reduction in cancer risks. The changes in cancer risks due to changes in PAH emissions could be considered in the screening risk assessment of the diesel exhaust, which is focused on a limited number of VOCs.

The addition of PIB leads to some significant increases in volatile organics. Some of these substances are also carcinogenic. The risk assessment illustrates increases in risks but expresses them on an absolute basis. The calculated risk increases are small (Tables 3 and 4). This is because they are based on average ambient outdoor air concentrations. This scenario does not adequately portray exposure conditions of exposed human populations that are subject to diesel exhaust. Nor does it take into account potential increases in use of the new formulation. Hence the risk assessment in Tables 3 and 4 provide little insights into the absolute or relative changes in risks. As a first approximation, the increases in VOCs in Table 1 and 2 provide a better indication of relative changes in cancer risk levels. I suggest that the risk estimates in Tables 3 and 4 are presented and evaluated both in terms of (i) relative changes in risk levels occurring as a result of Viscon & No-Viscon use and

(ii) absolute risk values calculated using more relevant exposure scenarios. The relative changes in risk due to reductions in PM and changes in hydrocarbon concentrations then need to be compared to determine the advantages of the new formulation. At this point, it is not clear whether Viscon provides a health benefit.

An additional comment on the risk assessment is the consideration of the potential health impacts of 1,3-butadiene. Viscon appears to increase 1,3-butadiene emissions by 16.4 fold (Table 4, p. 11). The US-EPA uses a reference concentration of 0.9 ppb, which may be in the range of realistic exposure conditions.

To complete the multi-media evaluation of Viscon, significant additional attention has to be paid to PIB. PIB is being portrayed as water insoluble, persistent and innocuous substances that requires little attention. However, it is important to recognize that global initiatives (i.e. UN Stockholm Convention on Persistent Organic Pollutants) and domestic legislation in the US (TSCA) as well as the REACH initiative in the European Union target poorly water soluble, persistent substances that are potentially harmful to the environment and human health. Although I am optimistic about PIB not being a problematic substance, it is important in a scientific assessment to support this with relevant information. The current evaluation provides little information. Hence, additional information in several areas is required to support a multi-media assessment.

First, it is important to provide a better characterization of PIB in the Viscon product and the reaction products that may be formed after combustion in diesel engines. The reports refer to different molecular weight ranges for PIB and the actual composition of the PIB is unclear. There are several commercial formulations of PIB with documented molecular weight ranges. Key questions that need to be addressed are: What are the PIBs that will be used in Viscon? What is the PIB composition in the diesel solution? How will the PIBs be affected by combustion? (e.g. are they broken down in lower molecular weight PIBs, butadienes and/or oxidative products)? What are the PIBs that will enter the environment? Without this information, it is hard to make credible conclusions on the multimedia environmental behaviour of this substance.

Second, the lack of information from biodegradation studies makes it difficult to assess the persistence of PIB. The report states that biodegradation studies are planned and that more information will become available. This is good. However, the stated "lack of methods to quantify concentrations of PIBs in environmental media" may pose significant challenges to obtaining this information. In my view, the authors make a reasonable assumption that PIB is likely very persistent. This can lead to the accumulation of PIBs in soils and sediment in the environment. The latter is a concern from a toxicological perspective as in most cases the "dose makes the poison" and higher concentrations can set the stage for greater impacts. However, natural processes like sediment and soil deposition or burial do provide natural "loss" mechanisms that will limit the concentrations that can ultimately be reached. This could be added to the assessment report to address concerns over an ever increasing concentration. Model simulations (e.g. Webster, E. and Mackay, D. 1998. Evaluating Environmental Persistence. Environ. Toxicol. Chem. 17: 2148-2158.) can be presented to support the effective loss of PIB from ecological systems. In the biodegradation studies, attention should also be paid to the formation of metabolites, which are likely of lower molecular weight than the original PIB formulation and hence can be more bioavailable for uptake in biota. An additional issue that should be considered is the breakdown of PIBs in the atmosphere after release in engine exhaust.

Third, the UN Stockholm Convention identifies long range atmospheric transport as an important measure in assessing the environmental impact of commercial chemicals. The evaluation of Viscon should address this issue since atmospheric transport of PIB on aerial particles is a real possibility.

Fourth, the discussion of the toxicity of PIB lists several studies involving oral and dermal exposure of very large amounts of PIB in mammals. I agree with the authors that the results are encouraging and do not demonstrate a high toxicity, but the exposure scenarios are not representative of PIB exposure from diesel exhaust. However, no studies are reported that involve aerial exposure. After combustion, PIB can be present at high concentrations on associated particulate materials in diesel exhaust and interact with lung tissues. Hence, aerial exposure should be investigated and considered in more detail.

In terms of aquatic toxicity, there is one reference that may be useful for the evaluation (Fingas, M.F., D.A. Kyle, N. Laroche, B. Fieldhouse, G. Sergy, and G. Stoodley Publication Year: 1995 Title: The Effectiveness Testing of Oil Spill-Treating Agents Source: In: P.Lane (Ed.), The Use of Chemicals in Oil Spill Response, ASTM STP 1252, Philadelphia, PA :286-298). It shows no acute aquatic toxicity at very high aqueous concentrations. I agree with the authors that PIB can be expected to have a very low aquatic toxicity.

Viscon Review 2010

Comments in this review are mostly limited to air emissions summaries and data as soil and water concerns are generally beyond the expertise of this reviewer.

Air Emissions and Public Health Evaluations: The overall conclusion that reduction in PM emissions in additive-treated diesel fuel appears correct on the surface. The summary tables report that the 25% reduction in PM is significant but it is somewhat offset by the increase in other pollutants including CO, NOx, and hydrocarbons. If one accepts the CARB statement that 70% of the adverse effects of air pollution are related to PM, then the use of Viscon-treated diesel fuel to reduce PM emissions appears warranted. One of the most impressive effects of the additive is the major reductions in carcinogenic PAH species. Overall, the MMWG's evaluation of the Viscon additive is correct in that the product is not likely to have significant impacts on the environment and there is a potential and important benefit in protecting human health if the product reduces PM emissions.

There are concerns, however, potentially major ones, in the supplied reports, that should be addressed. One concern is the overall conclusion that PM is actually reduced by the addition of Viscon. The emissions data were collected at the end of a dilution tunnel and the summary Table 2 presented in the Multimedia Evaluation of Viscon report shows that reductions in PM emissions are accompanied by increases in hydrocarbons and other gaseous pollutants. The evaluation lacks a discussion of the potential for these gases to undergo atmospheric chemistry changes which may result in their condensing onto airborne particles. Thus, although the PM emissions may be reduced at a short time point after the combustion process, the much greater mass of the gaseous pollutant emissions may nullify these reductions during natural 'aging' in the ambient air. A discussion of this issue would be important for the Multimedia Evaluation.

A second concern is related to the discussion of the increase in gaseous precursors to ozone. Although these increases might be important, they are apparently dismissed as being statistically insignificant. Figure 2 and the accompanying text clearly demonstrate that the variability in the ULSD baseline tests was very large (approximately 10-fold greater than during the other tests). It would appear that something went awry in the tests and, therefore, the discussion might focus less on statistical significance but whether the 2.5 to 3% increases in NOx and NO would impact ozone generation in ambient air. Such reasoning was used to address the relative importantce of a 6% increase in hydrocarbons in the last paragraph on page 12.

To this reviewer, the greatest concern with this Multimedia Evaluation is the summarization of the emissions test results. In the Tier III Summary report, Table 1 shows the actual emission test results of 2005 for a reference fuel, the candidate fuel, and the candidate fuel with Viscon. The test results appear to vary significantly over time and Table 1A confuses things even more – it appears that the candidate fuel with Viscon (instead of the candidate fuel only) was averaged with a reference fuel to get a reference fuel average that was used to calculate the reduction in PM emissions. Thus, there is a lack of confidence in the accuracy of the 2005 summarization for the low sulfur diesel tests (PM reduction would have been even greater because the candidate fuel's PM emissions were high). Oddly, the Multimedia

Evaluation discusses a 2003 and 2006 test but the detailed tables are clearly from 2005 so it is unclear what type of diesel fuel (LSD or ULSD) was used. Just as importantly, it is clear that the time-dependency of the test results may have skewed the findings. There was an 8% decrease in PM emissions for the reference fuel in the test conducted in early versus late June and for some reason the candidate fuel only (i.e., no Viscon additive) was tested 3 weeks before the candidate fuel with Viscon and only the reference fuel was tested on the same day as the candidate fuel with Viscon in late June. Similar detailed Tables for the 2007 (2008?) test data for ULSD must be carefully evaluated.

Therefore, the overall efficacy of the Viscon additive, while promising, needs to be more closely evaluated. The most promising data (presented in Table 3 found on page 4 of the Tier III Summary), in fact, shows that on-road vehicle emissions for PM and gaseous components are reduced across-the-board in one test.

Water Evaluation: The SWRCB staff's conclusions and recommendations are supported by the available test data and reports on Viscon.

Soil and Hazardous Waste Evaluation: The conclusions of the MMWG appear correct in that the Viscon additive will not have significant impacts on soil or waste.

Minor Concerns:

1. Definitions and abbreviations were somewhat confusing. There was no readily available definitions for pre-durability/post-durability or NMHC in the documents.
2. The storage method for Viscon is unclear based upon what is stated on pages 3 and 4 of the Multimedia Evaluation (can be stored underground in page 4 and not stored underground on page 3).
3. The working group's set of recommendations (page 10 of Multimedia Evaluation) are excellent and the combustion tests for on-road vehicle use would be necessary.
4. Many of the discussions of pre- and post-durability tests are confusing without knowing the details of the difference in pre- and post- (timing, etc.).
5. Table 5 states a 569% increase in m-tolualdehye although it went from 0.0000 to 0.000109.
6. Viscon Evaluation (Wednesday…..) states a molecular weight of 4 million whereas the Tier I report states 7 million for the additive.
7. The Tier I report concludes on page 7 that benefits would be accrued "due to demonstrated reductions in exhaust emissions of NOx, PM, CO, and HC." This

overstates (possibly incorrectly for the gaseous pollutants) the findings of the emissions test data.

Date: February 28, 2010

To: Floyd Vergara, Manager, Industrial Section, CARB
Aubrey Sideco, Air Resources Engineer, CARB

From: Miriam Diamond, PhD.
University of Toronto

Re: **Multimedia Evaluation of Viscon**

First, let me open by stating that I have not had any conversations with anyone regarding this review, other than with Aubrey Sideco requesting that I submit the review.

My review is based on my expertise in measuring chemicals in environmental media including air and soil, evaluating multimedia chemical fate and transport, and peripheral involvement in the regulatory arena (at Canadian provincial and federal levels).

I have reviewed the following documents:

- California Environmental Protection Agency, Multimedia Evaluation of Viscon, January 14, 2010
- CARB, Assessment of emissions of Viscon Diesel on Exhaust emissions from heavy-duty engines, January 14, 2010
- Attachment C, State Water Resources Control Board: Viscon Evaluation
- Attachment D, office of Environmental Health Hazard Assessment: Staff Report on Health Impacts of Viscon Diesel Fuel
- Attachment E, Department of Toxics Substances Control: Recommendation on Proposed Viscon Diesel
- Attachment F, Letter of Conditional Approval of Tier I and Tier II, May 19, 2009 and November 24, 2009
- Viscon Multi Media Evaluation (Tier I), October 24, 2008
- Viscon Multi Media Evaluation (Tier II), March 16, 2009
- Viscon Multi Media Evaluation (Tier III), June 3, 2009

BACKGROUND

There is no question about significant health concerns arising from diesel particulate emissions. A large and growing literature connects PM emissions from the transportation sector, and particularly diesel emissions, with a wide range of adverse health effects in human populations. Those especially affected live in proximity to heavily travelled highways, depots that service diesel vehicles, and occupationally exposed individuals. As such, there is a well justified motivation to reduce diesel PM emissions.

The proposal to add Viscon to diesel fuel in order to reduce PM emissions is a reasonable proposition. This proposal is modest in scope since Viscon would be added to only 0.2% of all diesel fuel sold in California. Its use would be restricted to off-road equipment. As I understand the situation, PM local emissions from off-road diesel equipment can be significant. However, it is important to closely scrutinize the proposal not only for local effects but also as this could be an in-road to the more widespread use of Viscon.

Viscon is an additive to diesel fuel consisting of 5 ppm polyisobutylene or PIB synthesized by BASF as Oppanol. PIB is polymerized by reacting 98% isobutylene with ~2% isoprene. PIB is registered for use as a food grade substance that is used in a very wide variety of applications. An aminated PIB has been added to diesel fuel as a detergent to reduce PM and hydrocarbon production by reducing the fowling of fuel injectors (Hammerle et al. 1994 Environ Health Perspec 102 Supple 14:25-30).

The intention of this review is to assess the multimedia evaluation of Viscon in the documents listed above. Attention is given to potential impacts that could result from the handling, storage and combustion of diesel fuel amended with Viscon.

The State of California's Multi Media Working Group identified two main knowledge gaps pertaining to Viscon's biodegradability and potential impact on soil cleanup.

OVERALL ASSESSMENT

Atmospheric Emissions

1. Combustion tests were conducted using Viscon-treated low and ultra low sulphur diesel (ULSD) fuel using the procedure ISO 8178C1. Emission changes with the Viscon-treated ULSD fuel found were:

- ~25% reductions in PM emissions
- Trivial changes in NO, CO and CO_2
- 6.2% increase in total hydrocarbons
- Increases in VOCs such as benzene, ethylbenzene, toluene and formaldehyde (from 2-43% depending on pre- or post-durability test)
- Decrease in acetaldehyde
- Decrease in most PAH (except dibenzo(*ah*+*ac*)anthracene)

Strangely missing from the Summary and the Health Impacts reports is the increased emission of 1,3-butadiene (1640%). The difference between baseline ULSD and Viscon-ULSD for 1,3-butadiene emissions is the largest of all chemicals measured, followed by m-tolualdehyde (nearly 1000% for post-durability test). If indeed PIB is synthesized with 2% isoprene, then the increased emission of 1,3-butadiene from Viscon-treated diesel is understandable since these two chemicals are closely related (differing by a methyl group). The significance of increased 1,3-butadiene emissions comes from its designation as a carcinogen emitted largely from gasoline and diesel vehicle emissions. These statements are excerpted from the CARB website:

> The ARB has identified 1,3-butadiene as a toxic air contaminant based on its potential to cause cancer. California has determined under Assembly Bill 1807 and Proposition 65 that 1,3-butadiene is a cancer-causing compound.
>
> Cancer risk is the number of excess cancer cases among a million people if the people are exposed to levels of a toxic air pollutant over 70 years. 1,3-butadiene represents approximately 20% of the potential cancer risk of the nine measured compounds, excluding diesel particulate matter. 1,3-butadiene represents approximately 4% of the potential cancer risk of the nine measured compounds and the estimated diesel particulate matter.
> http://www.arb.ca.gov/ch/aq_result/crockett/cr_buta.htm

It could well be that a risk assessment taking into account the decreased emissions of PM more than compensates for the increased emissions of 1,3-butadiene, however this needs to be explicitly addressed.

2. I find it odd that the Staff Report on Health Impacts of Viscon Diesel Fuel concludes that since high molecular weight PIB or HMWPIB will be in the particulate phase if released into air, that it would deposit on soil and surface water rather than staying airborne and subject to atmospheric transport. I was unable to find the diameter of Oppanol pellets but are they sufficiently large that all Oppanol, even as Viscon, would be subject to gravitational settling in close proximity to its point of atmospheric release? If so, then this needs to be explicitly stated rather than relying on a conclusion that does not consider particle size as a factor in atmospheric fate.

3. Further inspection of the emission test data is made difficult by its reporting using up to 6 digits after the decimal place. Detection limits are not reported and "no detects" are reported as zero – e.g., 0.00000000 :g/bhp-hr. This number suggests amazing analytical accuracy or a testing facility that hasn't figured out what detection limits and significant digits are.

It is bizarre that test results include the standard deviation for the baseline ULSD emissions but the covariance for the Viscon ULSD results. At best, the reporting of the covariance removes the ease of assessing whether differences between baseline and Viscon results are significantly different and at worst gives a false sense of accuracy to the Viscon ULSD emission data.

4. Since standard deviations of the combustion test data were recorded, then all baseline vs Viscon test results should be subject to statistical tests of significance, rather than reported as percent change. Percent change is not "statistical data" (e.g., page 10 of the Assessment of Emissions of Viscon Diesel on ….).

Since the results have not been subject to statistical analysis, any statements regarding small changes in emissions, such as those of a ~1% reduction in CO_2 emissions can only be taken with a grain of salt. The Summary Report should only comment on significant changes in baseline vs Viscon-treated fuel emissions.

Emissions to Land and Water

PIB is used to aid the clean up of oil spills by increasing fuel viscosity (probably used at much higher concentrations than 5 ppm!). PIB added at 70 ppm reduces the atomization of oil fluids (http://www.epa.gov/oppt/greenengineering/pubs/case_studies.html). The molecular weight of PIB suggests that it would behave as a colloid when released into surface or ground water, or soil.

5. It is unclear to me what the basis of the conclusion "… that PIB is not likely to travel further in soil or groundwater…" because of its insolubility and molecular weight. It seems quite possible to me that PIB could travel significant distances if diesel containing PIB was spilled as "free product" LNAPL (low density non-aqueous phase liquid) in a high porosity aquifer. Could PIB participate in colloidally-assisted transport of other constituents in the Viscon-treated diesel? How would the particle size of PIB affect its mobility in soil?

6. At lower volume spills, it seems that PIB would act as an excellent sorbent of oil as well as other constituents such as nutrients in soils and sediment. Presumably questions regarding its fate in soil and the impact of PIB on the availability of other soil constituents (such as nutrients) will be investigated in further work.

7. All reports seem to give groundwater migration and contamination short shrift. I recommend that implications regarding groundwater be further examined. My questions regarding soils and groundwater

support the further investigation of knowledge gaps regarding fate and transport in soil and potential impacts on soil clean up.

CONCLUSIONS

The results presented suggest that there is a net benefit of introducing Viscon-treated ULSD for use in off-road diesel applications. However, the reports do not allow one to make this conclusion with ease or with confidence. The Multimedia Evaluation of Viscon, that draws directly from reports from other boards, needs to explicitly list all potential benefits and dis-benefits of using Viscon-treated ULSD. Appropriate use of statistical testing is necessary to clarify what are and what are not real differences in test results that can be attributed to Viscon. The authors should not make untested assumptions (e.g., PIB "will remain at the point of release unless the soil is disturbed" p. 7 of summary report) or should clearly justify their logic and the data upon which their conclusions are based. Regarding emissions testing, all significant differences between non-Viscon-treated and Viscon-treated ULSD should be clearly reported, particularly the considerable increase in emissions of 1,3-butadiene, and to a lesser degree, non-methane hydrocarbons.

APPENDIX K

Multimedia Working Group Responses to Peer Review Comments
and
Individual Agency Responses to Comments

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Multimedia Workgroup Responses to Peer Review Comments

<u>1,3 butadiene</u>

A-1. Comment: It is noted that the average emission of 1,3,-butadiene, associated with Viscon containing diesel fuel, was reported to be 1,640% above the baseline [[1]; Table 4]. However, the MMWG did not consider health impacts associated with 1,3-butadiene; it is unclear 1,3-butadiene is being assessed by the MMWG as a non-toxic air pollutant. (Cohen, pg 3)

Comment: Strangely missing from the Summary and the Health Impacts reports is the increased emission of 1,3-butadiene (1640%). The difference between baseline ULSD and Viscon-ULSD for 1,3-butadiene emissions is the largest of all chemicals measured, followed by m-tolualdehyde (nearly 1000% for post-durability test). If indeed PIB is synthesized with 2% isoprene, then the increased emission of 1,3-butadiene from Viscon-treated diesel is understandable since these two chemicals are closely related (differing by a methyl group). The significance of increased 1,3-butadiene emissions comes from its designation as a carcinogen emitted largely from gasoline and diesel vehicle emissions. These statements are excerpted from the CARB website:

The ARB has identified 1,3-butadiene as a toxic air contaminant based on its potential to cause cancer. California has determined that under Assembly Bill 1807 and Proposition 65 1,3-butadiene is a cancer-causing compound. Cancer risk is the number of excess cancer cases among a million people if the people are exposed to levels of a toxic air pollutant over 70 years. 1,3-butadiene represents approximately 20% of the potential cancer risk of the nine measured compounds, excluding diesel particulate matter. 1,3-butadiene represents approximately 4% of the potential cancer risk of the nine measured compounds and the estimated diesel particulate matter. http://www.arb.ca.gov/ch/aq_result/crockett/cr_buta.htm. It could well be that a risk assessment taking into account the decreased emissions of PM more than compensates for the increased emissions of 1,3-butadiene, however this needs to be explicitly addressed. (Diamond, pg 2)

Comment: An additional comment on the risk assessment is the consideration of the potential health impacts of 1,3-butadiene. Viscon appears to increase 1,3-butadiene emissions by 16.4 fold (Table 4, p. 11). The US-EPA uses a reference concentration of 0.9 ppb, which may be in the range of realistic exposure conditions. (Gobas, pg 2)

Comment: First, the staff did not evaluate the potential impacts of the very significant increase in 1,3 butadiene reported in “Viscon Multi Media Evaluation (Tier III) Summary” prepared by Viscon California LLC. This summary finds a 1682% increase in 1,3 butadiene. The Staff Report on Health Impacts of Viscon Fuel (Dec. 2009) did not consider this potentially harmful compound. Given the composition of Viscon, it is not unexpected to see an increase in emissions of 1,3-butadiene. (Russell, pg 1)

Response: On average, 1,3-butadiene increased by approximately 770% from baseline (4.14 mg/bhp-hr increase). The staff report was revised with this corrected average value.

As reported in Table 4 of the revised staff report, pre-durability 1,3-butadiene data were below the detection limit, but post-durability data showed an increase of about 1,640% from baseline. In order to further assess the risk involved with such high post-durability increases, OEHHA conducted an additional risk assessment for 1,3-butadiene in diesel exhaust. Evaluated at the highest level of increase, the attributable lifetime cancer risk calculated from the increase is 2.5×10^{-8}. Therefore, even with the highest reported increase of 1,3-butadiene, the estimated risk is less than 1 in a million. (ARB)

The results of the assessment by OEHHA is as follows:

Screening risk assessment for 1,3-butadiene in diesel exhaust
An upper-bound estimate of lifetime cancer risk attributable to diesel exhaust from combustion of Viscon uses the amount of 1,3-butadiene in post-durability tests compared with the amount in baseline tests. The increase in emissions of 1,3-butadiene is 1,641%. The attributable risk calculated from this increase, from the average ambient level in Burbank, 0.283 ppb, and from the unit risk factor, 1.7×10^{-4} $(\mu g/m^3)^{-1}$, for 1,3-butadiene is 2.5×10^{-8}. (OEHHA)

Statistical Information

A-2. Comment: A second concern is related to the discussion of the increase in gaseous precursors to ozone. Although these increases might be important, they are apparently dismissed as being statistically insignificant. Figure 2 and the accompanying text clearly demonstrate that the variability in the ULSD baseline tests was very large (approximately 10-fold greater than during the other tests). It would appear that something went awry in the tests and, therefore, the discussion might focus less on statistical significance but whether the 2.5 to 3% increases in NOx and NO would impact ozone generation in ambient air. Such reasoning was used to address the relative importance of a 6% increase in hydrocarbons in the last paragraph on page 12. (Gordon, pg 1)

Response: The reviewer mistakenly compared the baseline standard deviation with the Viscon covariance values. The staff report was revised to include the standard deviations of the Viscon pre- and post-durability data instead of the covariance values between data sets.

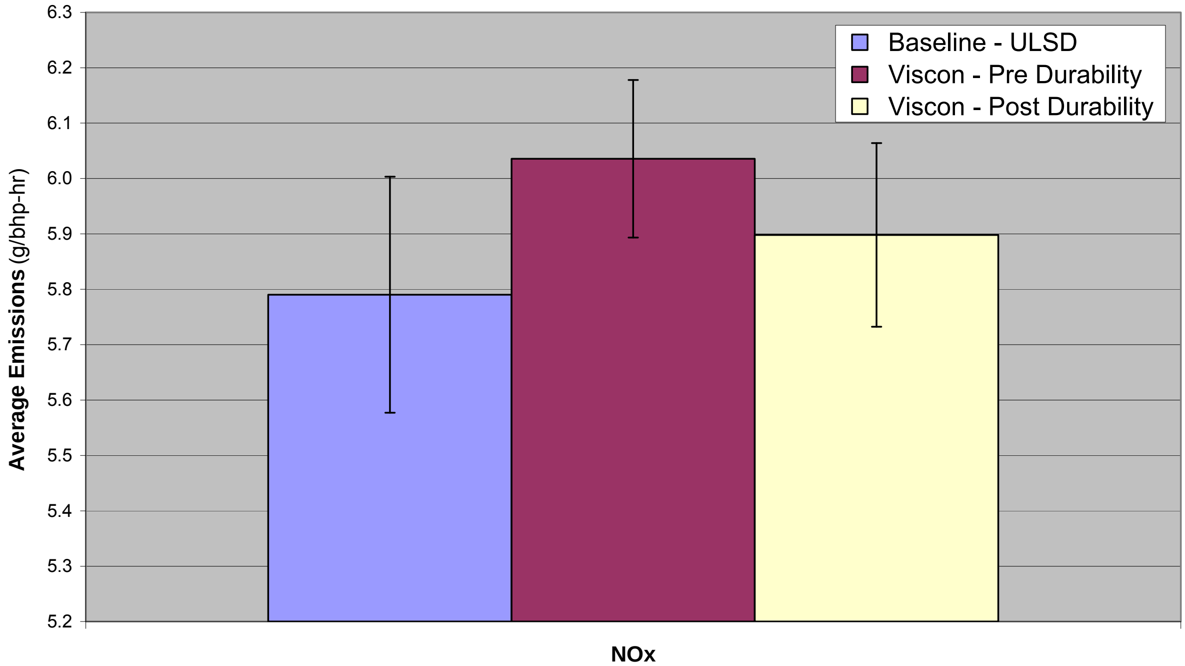
On average, test results from the testing of ozone precursors show a 2.9% increase in NOx and a 6.2% increase in HC emissions.

The test results, including percent changes and standard deviation values of each set of tests, were calculated and reported in the staff report. Staff did not determine specific thresholds of significance or relevance. The evaluation was based on the relative risk to impact air quality and emission level changes in the ambient air.

For NOx, average test results showed a 2.9% increase from baseline. A total increase of about 0.17 g/bhp-hr NOx was reported with high standard deviations of 0.213, 0.166, 0.142 for baseline, pre-durability, and post-durability tests, respectively.

Figure 2 is a graphical summary of the results from the baseline and Viscon pre- and post-durability tests. As shown in the figure, the standard deviation of each set of tests is illustrated by the error bars on the graph. The error bars show the relatively wide variability and spread between tests.

Figure 2. Comparison of Baseline and Viscon NOx Emission Results



Based on the NOx results, the calculated increase is not significantly representative because the error bars for the Viscon results overlap with the baseline results and the calculated t-score was greater than 0.05.

For NOx emission increases, current regulations allow for a ten percent increase for any product that is able to show a reduction of particulate matter levels by twenty-five percent or more.

Average HC emissions increased by 6.2 percent from baseline emissions levels. Some VOC emissions also increased. At the limited and controlled us of the Viscon additive, the increase in emissions would not significantly impact emission levels in the ambient air or air quality. (ARB)

A-3. Comment: In the CARB "Assessment of Emissions of Viscon Diesel on Exhaust Emissions from Heavy-Duty Engines", they note that the increase in NOx was not statistically significant. This brings up two issues. First, at what level is the increase not significant? (Russell, pg 1)

Response: The staff report was revised to include the standard deviation of the results instead of covariance. Please see response to comment A-2.

A-4. Comment: They further note that total HC increased by 6.2%. However, NMHC increased 54.3%. This would appear to be significant, and in need of greater consideration. (Russell, pg 2)

Response: The multimedia workgroup is aware of the discrepancy in the increases of HC versus NMHC but believe that initial NMHC testing experienced an error and therefore shall be disregarded in future publications once it is confirmed that there was a cause for the error. (ARB)

A-5. Comment: It is bizarre that test results include the standard deviation for the baseline ULSD emissions but the covariance for the Viscon ULSD results. At best, the reporting of the covariance removes the ease of assessing whether differences between baseline and Viscon results are significantly different and at worst gives a false sense of accuracy to the Viscon ULSD emission data. (Diamond, pg 3)

Comment: In Table 2 of "Assessment of Emissions of Viscon Diesel on Exhaust Emissions from Heavy-Duty Engines" they provide the covariances. This should be defined mathematically and a more complete discussion of its meaning would be useful. That table should also provide the standard deviations in the Pre and Post-durability tests. In Table 4 of that report, they do not note that there is a potential problem with the perdurability measurements of 1,3 butadiene. (Russell, pg 2)

Comment: Second, throughout the various evaluations, it would be useful to more completely show standard deviations (and adequately identify them as to what type, i.e., of the sample versus the mean). (Russell, pg 2)

Response: The staff report was revised to include the standard deviation of the results instead of covariance. Regarding the comments to statistical information, please see response to comment A-2. Regarding 1,3-butadiene, please refer to response to comment A-1.

A-6. Comment: Further inspection of the emission test data is made difficult by its reporting using up to 6 digits after the decimal place. Detection limits are not reported and "no detects" are reported as zero – e.g., 0.00000000 :g/bhp-hr. This number suggests amazing analytical accuracy or a testing facility that has not figured out what detection limits and significant digits are. (Diamond, pg 3)

Response: The tables in the staff report were revised to specify results below the detection limit as "*ND – Not Detected; Below detection limit*." The standard deviation and values that could not be calculated were specified as "NC – Not calculated." All other values were reported with three significant figures. (ARB)

A-7. **Comment:** Table 5 states a 569% increase in m-tolualdehye although it went from 0.0000 to 0.000109. (Gordon, pg 2)

Response: The results provided in Table 5 were rounded. The percent change is based on exact numbers and is correct.

	ULSD Avg (g/bhp-hr)	Viscon Pre-durability Avg (g/bhp-hr)	Percent Change
m-tolualdehyde	0.0000163333…	0.000109333…	569.387…% (ARB)

A-8. **Comment:** Since standard deviations of the combustion test data were recorded, then all baseline vs. Viscon test results should be subject to statistical tests of significance, rather than reported as percent change. Percent change is not "statistical data" (e.g., page 10 of the Assessment of Emissions of Viscon Diesel on…).

Since the results have not been subject to statistical analysis, any statements regarding small changes in emissions, such as those of a ~1% reduction in CO_2 emissions can only be taken with a grain of salt. The Summary Report should only comment on significant changes in baseline vs. Viscon-treated fuel emissions. (Diamond, pg 3)

Response: Staff conducted a statistical analysis of the results provided, including the calculation and evaluation of the standard deviation values and t-test data. Emission results that showed a significance increase were given further review to discover if there was cause for concern. Please also refer to response to comment A-2. (ARB)

Risk Assessment

A-9. **Comment:** The addition of PIB leads to some significant increases in volatile organics. Some of these substances are also carcinogenic. The risk assessment illustrates increases in risks but expresses them on an absolute basis. The calculated risk increases are small (Tables 3 and 4). This is because they are based on average ambient outdoor air concentrations. This scenario does not adequately portray exposure conditions of exposed human populations that are subject to diesel exhaust. Nor does it take into account potential increases in use of the new formulation. Hence, the risk assessment in Tables 3 and 4 provide little insights into the absolute or relative changes in risks. As a first approximation, the increases in VOCs in Table 1 and 2 provide a better indication of relative changes in cancer risk levels. I suggest that the risk estimates in Tables 3 and 4 are presented and evaluated both in terms of (i) relative changes in risk levels occurring because of Viscon & No Viscon use and (ii) absolute risk values calculated using more relevant exposure scenarios. The relative changes in risk due to reductions in PM and changes in hydrocarbon concentrations then need to be compared to determine the advantages of the new formulation. At this point, it is not clear whether Viscon provides a health benefit. (Gobas, pg 2)

Response: OEHHA agrees that using "more realistic" exposure scenarios would be helpful in understanding possible risks attributable to Viscon combustion. More specifically, it would be helpful to assess risks from facilities using diesel engines. This type of assessment requires information on distances between exhaust release points and receptor locations as well as duration of exposures at receptor locations. Unfortunately, this information is not available. (OEHHA)

Modeling all release scenarios would be difficult given the variability and range of tests that could be conducted. Detailed information on each source that will be using Viscon would be required to run more in-depth scenarios. If Viscon applies to expand their production and use of Viscon within the state, further testing scenarios will be evaluated. (ARB)

A-10. Comment: Fourth, the discussion of the toxicity of PIB lists several studies involving oral and dermal exposure of very large amounts of PIB in mammals. I agree with the authors that the results are encouraging and do not demonstrate a high toxicity, but the exposure scenarios are not representative of PIB exposure from diesel exhaust. However, no studies are reported that involve aerial exposure. After combustion, PIB can be present at high concentrations on associated particulate materials in diesel exhaust and interact with lung tissues. Hence, aerial exposure should be investigated and considered in more detail. (Gobas, pg 4)

Response: The multimedia working group considered various release scenarios, however, with limited resources, considering the worst-case scenario for exposure was the logical choice. The resulting high concentration exposure tests with minimal health effects provided the group with enough certainty that if PIB were accumulated over time, their effects would be no worse than the prescribed acute high dosage effects. Without studies directly related to the fate and air release scenario in question, the group made logical comparisons to other compounds in the exhaust to determine the possible interaction effects. (ARB)

<u>Polyisobutylene</u>

A-11. Comment: First, it is important to provide a better characterization of PIB in the Viscon product and the reaction products that may be formed after combustion in diesel engines. The reports refer to different molecular weight ranges for PIB and the actual composition of the PIB is unclear. There are several commercial formulations of PIB with documented molecular weight ranges. Key questions that need to be addressed are: What are the PIB that will be used in Viscon? What is the PIB composition in the diesel solution? How will the PIB be affected by combustion? (E.g., are they broken down in lower molecular weight PIB, butadienes and/or oxidative products)? What are the PIB that will enter the environment? Without this information, it is hard to make credible conclusions on the multimedia environmental behavior of this substance. (Gobas, pg 3)

Response: The multimedia working group discussed the issue between varying PIB molecular weights but finds there are no distinguishable differences between a low and ultra high PIB. Viscon will only be able to verify their PIB composition as tested in the multimedia examination. To narrow down the PIB concentration would be difficult as polymer chemistry results in a range of molecular weights dependent upon the reaction time. The PIB concentration in the solution will be 5ppm. One part of the 500 ppm PIB additive combined with 99 parts diesel. The PIB will be converted or consumed during the combustion process; however, there is no detailed information available that definitively outlines the combustion reaction partitions. (ARB)

A-12. Comment: Second, the lack of information from biodegradation studies makes it difficult to assess the persistence of PIB. The report states that biodegradation studies are planned and that more information will become available. This is good. However, the stated "lack of methods to quantify concentrations of PIB in environmental media" may pose significant challenges to obtaining this information. In my view, the authors make a reasonable assumption that PIB is likely very persistent. This can lead to the accumulation of PIB in soils and sediment in the environment. The latter is a concern from a toxicological perspective as in most cases the "dose makes the poison" and higher concentrations can set the stage for greater impacts. However, natural processes like sediment and soil deposition or burial do provide natural "loss" mechanisms that will limit the concentrations that can ultimately be reached. This could be added to the assessment report to address concerns over an ever-increasing concentration. Model simulations (e.g. Webster, E. and Mackay, D. 1998. Evaluating Environmental Persistence. Environ. Toxicol. Chem. 17: 2148-2158.) can be presented to support the effective loss of PIB from ecological systems. In the biodegradation studies, attention should also be paid to the formation of metabolites, which are likely of lower molecular weight than the original PIB formulation and hence can be more bioavailable for uptake in biota. (Gobas, pg 4)

Response: DTSC recommended Viscon California LLC to conduct laboratory tests for biodegradation and fate and transport because no evidence was presented on whether the Viscon additive adversely changes the behaviors of toxic diesel components in contaminated soils. Since PIB itself has very low toxicity, persistence of PIB does not appear to be an environmental concern. As the method of determining the concentration of PIB is currently not available, it is not realistic to measure the efficiency of cleanup of PIB. However, it is necessary to understand whether adding PIB in diesel will or will not cause any further difficulties during cleanup of Viscon diesel spills compared to the cleanup of regular CARB diesel spills. DTSC suggested that the laboratory test be designed as a comparison of the fate and transport behaviors between Viscon diesel and CARB diesel. The goal of the laboratory test was to study potential impact of Viscon additive on the biodegradation and fate and transport of toxic diesel components in soils. Based on the test results, an analysis regarding the feasibility of soil cleanup of Viscon diesel should be provided. (DTSC)

A-13. Comment: In the Viscon formulation, PIB is dissolved in CARB diesel at concentration at 1% by wt. The resulting fuel mixture is then added to diesel fuel in which PIB is then at a concentration of less than ~5 ppm. High molecular weight (MW) PIB, as most high MW polymers, when dissolved in a suitable solvent, increases the shear viscosity of the solution and imparts viscoelastic behavior to the resulting solution [9-15]. One would expect that the viscosity of the resulting diesel fuel mixture (i.e., containing Viscon) would increase relative to CARB diesel. A Viscon viscosity of 0.5797 (g/cm·s) relative to 0.0233 (g/cm·s) for CARB diesel was reported at shear rate of 1,800 s^{-1} ([2, 3], Section III-D.2II). A Viscon viscosity of ~0.44-0.48 (g/cm·s) was reported[1] for shear rate of 250 s^{-1}. The above behavior is inconsistent with the expected shear-thinning behavior of polymer solutions. Extensional viscosity (obtained from oscillatory measurements) was provided for an alternate polymer but not for the specific PIB used in the Viscon additive. The assessment of the viscosity behavior, as reported in the Tier I [2] and Tier II [3] reports, is imprecise and it is worth noting the following:

Shear viscosity of PIB solutions would be expected to decrease with increasing shear. Extensional viscosity could increase with the extensional deformation rate (or elongational strain rate). Such effects are not temporary, but are sustained as long as the shear rate or elongational strain rate are maintained.

The zero-shear viscosity or viscosity at low shear (significantly less than the 1,800 s^{-1} cited in the Tier I Report [2]) is the viscosity relevant to evaluating the transport of Viscon or Viscon containing CARB diesel in soil and water.

Viscosity information for Viscon or diesel fuel containing Viscon was not available in the documents provided to the reviewer. Data on viscosity and viscoelastic behavior were provided for a product claimed to be similar (Elastosol; Attachments 9 and 10, [2]); it is unclear if the two products are of the same molecular weight. (Cohen, pg 2)

Response: DTSC has requested Viscon California LLC to conduct laboratory tests, including biodegradation and fate and transport. If transport rates of CARB diesel and Viscon diesel show significant difference, viscosity estimates of Viscon additive and Viscon diesel will be a good explanation for the difference, it is not necessary to study on the viscosity. (DTSC)

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[1] Note: 1 mPa·s = 1cP = 0.01 g/cm·s

A-14. Comment: The degradation of PIB under environmental conditions is slow (years). It is a polymer that is not readily oxidized or biodegraded. However, specific degradation half-lives (under typical environmental conditions) for the high MW PIB used in Viscon have not been provided. (Cohen, pg 2)

Response: PIB is known to be nonreactive under normal environmental conditions and of low toxicity. Although degradation half-life is an important property, it may be unrealistic to conduct tests to determine their respective half-lives in actual environmental conditions. However, the key is to understand how different these two products (Viscon Diesel and CARB Diesel) behave in soils regarding the fate and transport, or to understand whether there is a significant difference between these two products regarding their fate and transport behaviors in soils, which may impact their cleanups when spills occur. (DTSC)

<u>Atmospheric Transport</u>

A-15. Comment: Third, the UN Stockholm Convention identifies long-range atmospheric transport as an important measure in assessing the environmental impact of commercial chemicals. The evaluation of Viscon should address this issue since atmospheric transport of PIB on aerial particles is a real possibility. (Gobas, pg 4)

Response: The multimedia working group considered the long range atmospheric transport effects. However, the research surrounding atmospheric chemistry transport is limited and cannot assuredly affirm how PIB will react. Current literature suggests that observable concentrations of PIB are non-toxic and will react minimally while undergoing biodegradation. The MMWG considers that Viscon use being minimal in supply and locations of use will limit the short-term acute effects that may arise. Further evaluation of long-term transportation and accumulation of PIB in the atmosphere may be considered. (ARB)

A-16. Comment: I find it odd that the Staff Report on Health Impacts of Viscon Diesel Fuel concludes that since high molecular weight PIB or HMWPIB will be in the particulate phase if released into air, that it would deposit on soil and surface water rather than staying airborne and subject to atmospheric transport. I was unable to find the diameter of Oppanol pellets but are they sufficiently large that all Oppanol, even as Viscon, would be subject to gravitational settling in close proximity to its point of atmospheric release? If so, then this needs to be explicitly stated rather than relying on a conclusion that does not consider particle size as a factor in atmospheric fate. (Diamond, pg 3)

Response: The multimedia workgroup concluded that PIB would deposit on soil and water surfaces because of the non-polarity of the product and shear density of the molecule. PIB based on their density have a low vapor pressure, which would limit their ability to evaporate into the gas phase. Therefore, PIB movement would be limited to soil and water matrices. (ARB)

It was not the intention of OEHHA to imply that HMWPIB will not be transported in the atmosphere. Following release into air, winds will transport HMWPIB. However, this PIB will be associated with airborne particles. The distance that these particles travel before being deposited on water or soil will depend on many factors including particle size and meteorological condition. (OEHHA)

Soil and Water Transport

A-17. Comment: Quantitative information regarding soil infiltration and sorption of PIB (from Viscon or Viscon containing diesel fuel) was not provided. The viscosity of Viscon and diesel fuel containing the Viscon additive formulation will reduce the mobility of these fluid mixtures. Therefore, a specific evaluation of the efficacy soil cleaning methods may be warranted to assess the effect of viscosity as well as viscoelasticity. Another issue that requires attention is the sorption of PIB onto soil particles and the effect of soil organic carbon on such partitioning.

The spreading of Viscon or Viscon containing diesel on water (e.g., as a result of a spill) is likely to be less than for diesel given the higher shear viscosity and viscoelasticity of these formulations. It is possible that spreading of an oil slick may be also impacted by a change in the surface tension due to the presence of PIB; however, surface tension information was not provided regarding the surface tension of Viscon or CARB diesel containing Viscon. (Cohen, pg 3)

Response: Many properties of a contaminant will affect soil cleanup, including viscosity, partition coefficient, surface tension, etc. It is not necessary to determine every property that may affect the fate and transport of Viscon diesel in soil and water prior to a fate and transport comparison test. If the fate and transport of Viscon diesel is significantly different with the CARB diesel, further research on PIB and Viscon diesel may be required. (DTSC)

Given the concentration of PIB in Viscon diesel of 5 ppm, and the relatively small amount of Viscon diesel approved for use in the ARB verification process, the Water Board staff does not feel further research into the impacts of PIB on soil carbon portioning justified. (SWRCB)

A-18. Comment: The spreading of Viscon or Viscon containing diesel on water (e.g., because of a spill) is likely to be less than for diesel given the higher shear viscosity and viscoelasticity of these formulations. It is possible that spreading of an oil slick may be also impacted by a change in the surface tension due to the presence of PIB; however, surface tension information was not provided regarding the surface tension of Viscon or CARB diesel containing Viscon. (Cohen, pg 3)

Response: Fate and transport comparison tests are required to be conducted according to the conditional approval of the Tier I and Tier II reports. With these tests it is not necessary to determine every property that may affect the fate and transport of Viscon diesel in the environment. (ARB)

According to *"__Fingas, M.F., D.A. Kyle, N. Laroche, B. Fieldhouse, G. Sergy, and G. Stoodley Publication Year: 1995 Title: The Effectiveness Testing of Oil Spill Treating Agents Source: In: P.Lane (Ed.), The Use of Chemicals in Oil Spill Response, ASTM STP 1252, Philadelphia, PA :286,298__"* the surface tension of PIB contributes to the containment of oil released into the environment. The SWRCB staff considers this a positive characteristic. (SWRCB)

A-19. Comment: It is unclear to me what the basis of the conclusion "… that PIB is not likely to travel further in soil or groundwater…" because of its insolubility and molecular weight. It seems quite possible to me that PIB could travel significant distances if diesel containing PIB was spilled as "free product" LNAPL (low density non-aqueous phase liquid) in a high porosity aquifer. Could PIB participate in colloidally-assisted transport of other constituents in the Viscon-treated diesel? How would the particle size of PIB affect its mobility in soil? (Diamond, pg 3)

Response: The characteristics of PIB, such as high viscosity and insolubility in water, may result in PIB not traveling significant distances into soil or groundwater if spills occur. It is possible that PIB will travel further in light non-aqueous phase liquid (LNAPL) contaminated soil. However, there is no data to prove these assumptions. Therefore, DTSC requested Viscon California LLC to conduct a fate and transport test in order to observe the mobility of Viscon diesel in soils, compared with the mobility of CARB diesel. DTSC did not request Viscon California LLC to test PIB transport in soils because PIB itself is not a chemical of concern in this study.

The particle size of PIB may not be important because PIB dissolves into diesel as Viscon additive. The molecular weight of PIB used in the laboratory tests should be within a given range as used in the field. This is the factor that needs to be considered in the test design. (DTSC)

A-20. Comment: All reports seem to give groundwater migration and contamination short shrift. I recommend that implications regarding groundwater be further examined. My questions regarding soils and groundwater support the further investigation of knowledge gaps regarding fate and transport in soil and potential impacts on soil clean up. (Diamond, pg 3)

Response: DTSC has requested Viscon California LLC to submit a technical report that describes Viscon's potential impact on common soil cleanup methods based on the fate and transport test results. (DTSC)

A-21. Comment: At lower volume spills, it seems that PIB would act as an excellent sorbent of oil as well as other constituents such as nutrients in soils and sediment. Presumably, questions regarding its fate in soil and the impact of PIB on the availability of other soil constituents (such as nutrients) will be investigated in further work. (Diamond, pg 3)

Response: DTSC requested Viscon California to conduct a biodegradation test and a fate and transport test on the Viscon diesel, which will provide some information regarding if the Viscon additive enhances or prohibits biomass growth compared to CARB diesel. (DTSC)

<u>Atmospheric Chemistry</u>

A-22. Comment: The evaluation lacks a discussion of the potential for these gases to undergo atmospheric chemistry changes, which may result in their condensing onto airborne particles. Thus, although the PM emissions may be reduced at a short time point after the combustion process, the much greater mass of the gaseous pollutant emissions may nullify these reductions during natural 'aging' in the ambient air. A discussion of this issue would be important for the Multimedia Evaluation. (Gordon, pg 1)

Comment: Secondary organic aerosols in emissions raise a valid concern and pertain to both the Viscon fuel additive and baseline diesel. Our current regulatory framework treats primary PM, as measured using dilution samplers, as nonvolatile. Current studies, however, show that such primary PM from combustion sources contains a significant organic fraction of semi volatile species. Under atmospheric dilution, these species may initially evaporate from the particles and later condense back onto particles, depending on atmospheric concentrations, temperature and reactions with ozone and radicals. In addition to these semi volatile compounds in primary PM, the gaseous portion of emissions also contains a range of compounds with different volatilities and atmospheric reaction rates. These species may undergo atmospheric reactions that lower their volatility, and cause condensation on existing particles. Research in this area is rapidly advancing and ARB is supporting a project on by Carnegie Mellon University in which researchers will utilize a transportable smog chamber to perform experiments on the gas-particle partitioning of fresh emissions, and photochemical aging and secondary organic aerosol (SOA) formation from vehicle emissions. (Please see the work and references in the paper "Atmospheric organic particulate matter: From smoke to secondary organic aerosol," Neil M. Donahue, Allen L. Robinson, Spyros N. Pandis in Atmospheric Environment 43 (2009) 94–106.)

In short, the question of how to link tailpipe emissions to ambient particulate concentrations is poorly understood with respect to semi volatile organic species from combustion sources. The tests with the additive Viscon indicate that emissions of primary PM are lowered and hydrocarbons are increased. Without further knowledge about the volatility distribution of baseline and Viscon treated diesel emissions, and how atmospheric reactions change these distributions, little can be said about the comparative aged emissions. Some of these questions should be answered by the upcoming CMU project. (ARB)

Engine Selection

A-23. Comment: A second concern is that only one engine was used in this testing. Different engines can respond differently to fuel changes, and in-use engines can respond differently than test engines, so the results found should only be viewed as supportive for a providing a potential reduction in PM. On the other hand, those results, along with other studies using other organic additives to diesel fuel at such low levels, that one should expect little significant increase in NOx or CO. Thus, the finding that using Viscon as an additive to diesel in off-road application likely poses little threat for increasing NOx or CO is quite reasonable. However, I would like to see more engines tested before being comfortable saying that a significant decrease would be found in diesel PM emissions from using Viscon as a fuel additive. (Russell, pg 1)

Response: The emissions tests completed will merit verification of the Viscon additive for use with unregulated Caterpillar 3306 heavy-duty diesel engines.

The verification procedure requires at least one engine be tested to represent the emissions control group. Durability testing requirements state that the engine and application used in the durability demonstration must be representative of the emission control group for which verification is sought. (ARB)

Lubrication Oil Effects

A-24. Comment: Given that a fraction of the diesel PM emissions is due to partial combustion of lubrication oil, it would have been of interest to see an analysis of what fraction of the diesel PM was being reduced, and the mechanism of reduction. While the major physical attribute that is discussed in the documents is its impact on viscosity under shear, this does not directly imply anything about its combustion characteristics, and if its use would decrease PM formation from lubricating oil partial combustion. (Russell, pg 1)

Reponse: While the verification multimedia testing goes through some very in-depth procedures, a study of this caliber would be outside the scope of work. The working group feels that such a study such may be helpful for future applications. However, the resources are not available at this time to conduct such testing. (ARB)

Efficacy of Viscon

A-25. Comment: Therefore, the overall efficacy of the Viscon additive, while promising, needs to be more closely evaluated. The most promising data (presented in Table 3 found on page 4 of the Tier III Summary), in fact, shows that on-road vehicle emissions for PM and gaseous components are reduced across-the-board in one test. (Gordon, pg 2)

Response: Table 3 (Viscon Tier III Summary Report, pg 4) provides the results from a project carried out by the State of Texas through a grant from the Texas Commission on Environmental Quality (TCEQ). The results of the project by the State of Texas were provided in addition to the results from verification testing, conducted in accordance with the verification procedure (Title 13, California Code of Regulations, section 2700 et seq.). As documented in the July 2005 Final Report by Olson-EcoLogic Engine Testing Laboratory (attachment 1 of the Viscon Tier III Summary Report), the objective of the project was to show exhaust emission equivalency between a candidate fuel treated with the Viscon additive and the TxLed reference specification fuel when tested by the official EPA transient cycle emission test protocol. The test protocol was reviewed by the TCEQ and the US EPA but is different from the verification test protocol approved by the ARB. (ARB)

Storage

A-26. Comment: The storage method for Viscon is unclear based upon what is stated on pages 3 and 4 of the Multimedia Evaluation (can be stored underground in page 4 and not stored underground on page 3). (Gordon, pg 2)

Response: The statement on page 4 is a requirement set forth by the multimedia working group and is different from the production information provided by Viscon California.

Staff further clarifies the following: The statements on page 3 are information provided by the applicant. Viscon California LLC states that the Viscon additive is not stored in USTs and that Viscon treated diesel may be stored in USTs. Therefore, Viscon California does not store the additive in USTs but after production, Viscon treated diesel fuel may be stored in USTs. Different from the statement on page 3, the statement on page 4 sets forth a requirement. The requirement applies to current and future supplies and requires both the Viscon additive and Viscon diesel fuel to be stored in USTs that are compliant to state and federal regulations. (ARB)

Pre- and Post- Durability

A-27. Comment: Definitions and abbreviations were somewhat confusing. There were no readily available definitions for pre-durability/post-durability or NMHC in the documents. (Gordon, pg 2)

Response: The staff report was revised with more details about durability testing and requirements set forth in the verification procedure. Also, summary details regarding non-methane hydrocarbons (NMHC) were deleted from the staff report. (ARB)

A-28. Comment: Many of the discussions of pre- and post-durability tests are confusing without knowing the details of the difference in pre- and post- (timing, etc.). (Gordon, pg 2)

Response: The staff report was revised to include an additional section on pre- and post-durability. Pre-durability and post-durability tests were conducted under the same conditions and test methods as baseline testing. Pre-durability testing occurred after the engine and the Viscon fuel additive completed a de-greening period of 25 to 125 hours. This time frame allows an engine to reach a semi-steady state condition in which the device can be actively incorporated into the system and ensure that emission reductions are the result of the DECS and not a cleansed engine.

Post-durability testing occurred after the engine and fuel additive accrued an additional 1,000 hours of run time. This testing represents a portion of the engine's durable life. Post-durability testing allows for the reasonable assurance that the DECS is robust and will maintain the verified level of emission reductions over time.

The average of the pre- and post-durability test results were used to generate the net effect of the emission control strategy. An equal weight was given to each value before comparison to baseline results were made. (ARB)

<u>Emissions Data</u>

A-29. Comment: To this reviewer, the greatest concern with this Multimedia Evaluation is the summarization of the emissions test results. In the Tier III Summary report, Table 1 shows the actual emission test results of 2005 for a reference fuel, the candidate fuel, and the candidate fuel with Viscon. The test results appear to vary significantly over time and Table 1A confuses things even more – it appears that the candidate fuel with Viscon (instead of the candidate fuel only) was averaged with a reference fuel to get a reference fuel average that was used to calculate the reduction in PM emissions. Thus, there is a lack of confidence in the accuracy of the 2005 summarization for the low sulfur diesel tests (PM reduction would have been even greater because the candidate fuel's PM emissions were high). Oddly, the Multimedia Evaluation discusses a 2003 and 2006 test but the detailed tables are clearly from 2005 so it is unclear what type of diesel fuel (LSD or ULSD) was used. Just as importantly, it is clear that the time-dependency of the test results may have skewed the findings. There was an 8% decrease in PM emissions for the reference fuel in the test conducted in early versus late June and for some reason the candidate fuel only (i.e., no Viscon additive) was tested 3 weeks before the candidate fuel with Viscon and only the reference fuel was tested on the same day as the candidate fuel with Viscon in late June. Similar detailed Tables for the 2007 (2008?) test data for ULSD must be carefully evaluated. (Gordon, pg 1)

Response: The summary of the emissions test results were provided in the Viscon Tier II Report (*Viscon MultiMedia Evaluation Tier II Report, attachment 8)*. Tables 1 and 1A are the summary tables of the Viscon pre-durability testing conducted in October 2006. Table 1 provides the emission results for the baseline fuel, ULSD, and the candidate Viscon diesel fuel. The candidate fuel is ULSD with Viscon additive. Therefore, the reviewer mistakenly refers to two different candidate fuels: the candidate fuel and the candidate fuel with Viscon.

As described in the staff report (*Multimedia Evaluation of Viscon, p2)*, Viscon is a fuel additive that consists of one part ultra high molecular weight PIB and 99 parts ULSD. The Viscon additive would be used at a dose rate of approximately 500 ppm in diesel fuel. Therefore, the PIB content in Viscon treated diesel is about 5 ppm. (ARB)

A-30. Comment: The Tier I report concludes on page 7 that benefits would be accrued "due to demonstrated reductions in exhaust emissions of NOx, PM, CO, and HC." This overstates (possibly incorrectly for the gaseous pollutants) the findings of the emissions test data. (Gordo, pg 2)

Response: Verification test results show emission reductions in PM and CO2 (25% and 1.3%, respectively) but increases in NOx, HC, and CO (2.9%, 6.2%, and 1.4% respectively). (ARB)

Aquatic Toxicity

A-31. Comment: In terms of aquatic toxicity, there is one reference that may be useful for the evaluation (Fingas, M.F., D.A. Kyle, N. Laroche, B. Fieldhouse, G. Sergy, and G. Stoodley Publication Year: 1995 Title: The Effectiveness Testing of Oil Spill Treating Agents Source: In: P.Lane (Ed.), The Use of Chemicals in Oil Spill Response, ASTM STP 1252, Philadelphia, PA :286□298). It shows no acute aquatic toxicity at very high aqueous concentrations. I agree with the authors that PIB can be expected to have a very low aquatic toxicity. (Gobas, pg 5)

Response: The article recommended by Prof. Gobas presents the results of laboratory effectiveness' tests involving four classes of oil spill-treating agents. Two tables show side-by-side the effectiveness and the aquatic toxicity test results for thirteen solidifiers, and for sixty-one surface washing agents. The aquatic toxicity was estimated as 96-hour LC_{50} tested on Rainbow Trout and was expressed in mg chemical per liter of water.

To evaluate the appropriateness of the aquatic toxicity test results presented in the article to the VISCON additive, information about the chemical structure similarity between the article chemicals and the VISCON additive is needed. Since the article refers to the chemicals by their trade names only, OEHHA performed on-line search to obtain the necessary chemical structure data. Chemical structure information for all chemicals was either unavailable, either referred to as proprietary or trade secret. However, one of the solidifiers shown in Table 1 of the article – Elastol (a polyisobutylene with a lower molecular weight than the VISCON additive) was referred by VISCON as analog to the VISCON additive in the Tier II report. Assuming this, its

96-hour LC_{50} of > 5.600 mg/L may be considered in the evaluation of the VISCON additive. (OEHHA)

Overall Evaluation

A-32. Comment: *Soil and Hazardous Waste Evaluation:* The conclusions of the MMWG appear correct in that the Viscon additive will not have significant impacts on soil or waste." (Gordon, pg 2)

Response: The MMWG did not provide any conclusions regarding the soil evaluation; rather the MMWG requested further tests to fill in knowledge gaps identified by the working group. (DTSC)

Linda S. Adams
Secretary for
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Department of Toxic Substances Control

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Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Stephen d'Esterhazy
Air Pollution Engineer
California Air Resources Board

FROM: Li Tang. Ph.D., P.E.
Multimedia Products Section
Toxics in Products Branch

Yun Zhang, P.G.
Geological Support Branch

VIA: Caroline Rudolph, Chief
Multimedia Products Section
Toxics in Products Branch

Sherri Lehman, Chief
Toxics in Products Branch
Department of Toxic Substances Control

SUBJECT: Response to Peer Reviewer Comments on Multimedia Evaluation of Viscon Diesel

DATE: May 17, 2010

The California Department of Toxic Substances Control (DTSC) reviewed the following peer review reports related to the Multimedia Team evaluation of Viscon diesel and provides responses to the peer reviewers' comments specifically related to DTSC's areas of expertise as provided as a member of the Multimedia Team; i.e., hazardous waste management and soil cleanup issues. DTSC reviewers were Li Tang and Yun Zhang.

I. "Tier II and Tier III Multimedia Assessments of Viscon" prepared by Frank A.P.C. Gobas, Ph.D., Simon Fraser University dated February 2, 2010.

Comment:

"Second, the lack of information from biodegradation studies makes it difficult to assess the persistence of PIB. The report states that biodegradation studies are planned and that more information will become available. This is good. However, the stated "lack of methods to quantify concentrations of PIBs in environmental media" may pose significant challenges to obtaining this information. In my view, the authors make a reasonable assumption that PIB is likely very persistent. This can lead to the accumulation of PIBs in soils and sediment in the environment. The latter is a concern from a toxicological perspective as in most cases the "dose makes the poison" and higher concentrations can set the stage for greater impacts. However, natural processes like sediment and soil deposition or burial do provide natural "loss" mechanisms that will limit the concentrations that can ultimately be reached. This could be added to the assessment report to address concerns overran ever increasing concentration...."

Response:

DTSC recommended Viscon LLC conduct laboratory tests for biodegradation and fate and transport because no evidence was presented on whether the Viscon additive adversely changes the behaviors of toxic diesel components in contaminated soils. Since PIB itself has very low toxicity, persistence of PIB does not appear to be an environmental concern. As the method of determining the concentration of PIB is currently not available, it is not realistic to measure the efficiency of cleanup of PIB. However, it is necessary to understand whether adding PIB in diesel will or will not cause any further difficulties during cleanup of Viscon diesel spills, compared to the cleanup of regular CARB diesel spills. DTSC suggested that the laboratory test be designed as a comparison of the fate and transport behaviors between Viscon diesel and CARB diesel. The goal of the laboratory test was to study potential impact of Viscon additive on the biodegradation and fate and transport of toxic diesel components in soils. Based on the test results, an analysis regarding the feasibility of soil cleanup of Viscon diesel should be provided.

II. " Multimedia Evaluation of Viscon" prepared by Armistead G. Russell, Ph.D., Georgia Power Distinguished Professor of Environmental Engineering, Georgia Institute of Technology, [CARB received Feb 21, 2010].

No response required of DTSC.

III. " Multimedia Evaluation of VISCON Diesel Fuel Additive" prepared by Yoram Cohen, Ph.D., Professor, University of California Los Angeles, [CARB received Feb 18, 2010].

Comment:

"Viscosity information for Viscon or diesel fuel containing Viscon was not available in the documents provided to the reviewer. Data on viscosity and viscoelastic behavior were provided for a product claimed to be similar (Elastosol; Attachments 9 and 10, [2]); it is unclear if the two products are of the same molecular weight..."

Response:

DTSC has requested Viscon LLC to conduct laboratory tests, including biodegradation and fate and transport. If transport rates of CARB diesel and Viscon diesel show significant difference, viscosity estimates of Viscon additive and Viscon diesel will be a good explanation for the difference, it is not necessary to study on the viscosity.

Comment:

"The degradation of PIB under environmental conditions is slow (years). It is a polymer that is not readily oxidized or biodegraded. However, specific degradation half-lives (under typical environmental conditions) for the high MW PIB used in Viscon have not been provided..."

Response:

PIB is known to be nonreactive under normal environmental conditions and of low toxicity. Although degradation half-life is an important property, it may be unrealistic to conduct tests to determine their respective half-lives in actual environmental conditions. However, the key is to understand how different these two products (Viscon Diesel and CARB Diesel) behave in soils regarding the fate and transport, or to understand whether there is significant difference between these two products regarding their fate and transport behaviors in soils, which may impact their cleanups when spills occur.

Comment:

"Quantitative information regarding soil infiltration and sorption of PIB (from Viscon or Viscon containing diesel fuel) was not provided. The viscosity of Viscon and diesel fuel containing the Viscon additive formulation will reduce the mobility of these fluid mixtures. Therefore, a specific evaluation of the efficacy soil cleaning methods may be warranted to assess the effect of viscosity as well as viscoelasticity. Another issue that requires attention is the sorption of PIB onto soil particles and the effect of soil organic carbon on such partitioning.

The spreading of Viscon or Viscon containing diesel on water (e.g., as a result of a spill) is likely to be less than for diesel given the higher shear viscosity and viscoelasticity of these formulations. It is possible that spreading of an oil slick may be also impacted by a change in the surface tension due to the presence of PIB; however, surface tension information was not provided regarding the surface tension of Viscon or CARB diesel containing Viscon..."

<u>Response:</u>

Many properties of a contaminant will affect soil cleanup, including viscosity, partition coefficient, surface tension, etc. It is not necessary to determine every property that may affect the fate and transport of Viscon diesel in soil and water prior to a fate and transport comparison test. If the fate and transport of Viscon diesel is significantly different with the CARB diesel, further research on PIB and Viscon diesel may be required.

<u>IV. "Viscon Review 2010" prepared by Terry Gordon, Ph.D., Professor, New York University Langone, Medical Center, [CARB received Feb 17, 2010].</u>

<u>Comment:</u>

"Soil and Hazardous Waste Evaluation: The conclusions of the MMWG appear correct in that the Viscon additive will not have significant impacts on soil or waste..."

<u>Response:</u>

MMWG did not provide any conclusion regarding the soil evaluation; rather the MMWG requested further tests to fill the knowledge gap.

<u>V. "Multimedia Evaluation of Viscon" prepared by Miriam Diamond, Ph.D., Professor, Simon Fraser University, dated February 28, 2010.</u>

<u>Comment:</u>

"It is unclear to me what the basis of the conclusion… that PIB is not likely to travel further in soil or groundwater…because of its insolubility and molecular weight. It seems quite possible to me that PIB could travel significant distances if diesel containing PIB was spilled as "free product" LNAPL (low density non-aqueous phase liquid) in a high porosity aquifer. Could PIB participate in colloidally-assisted transport of other constituents in the Viscon-treated diesel? How would the particle size of PIB affect its mobility in soil?..."

Response:

The characteristics of PIB, such as high viscosity and insolubility in water, may result in PIB not traveling significant distances into soil or groundwater if spills occur. It is possible that PIB will travel further in light non-aqueous phase liquid (LNAPL) contaminated soil. However, there is no data to prove these assumptions. Therefore, DTSC requested Viscon LLC conduct a fate and transport test in order to observe the mobility of Viscon diesel in soils, compared with the mobility of CARB diesel. DTSC did not request Viscon LLC test PIB transport in soils because PIB itself is not a chemical of concern in this study.

The particle size of PIB may not be important because PIB dissolves into diesel as Viscon additive. The molecular weight of PIB used in the laboratory tests should be within a given range as used in the field. This is the factor that needs to be considered in the test design.

Comment:

"At lower volume spills, it seems that PIB would act as an excellent sorbent of oil as well as other constituents such as nutrients in soils and sediments. Presumably questions regarding its fate in soil and the impact of PIB on the availability of other soil constituents (such as nutrients) will be investigated in further work…."

Response:

DTSC requested Viscon to conduct a biodegradation test and a fate and transport test on the Viscon diesel, which will provide some information regarding if the Viscon additive enhances or prohibits biomass growth, comparing with the CARB diesel.

Comment:

"All reports seem to give groundwater migration and contamination short shrift. I recommend that implications regarding groundwater be further examined. My questions regarding soils and groundwater support the further investigation of knowledge gaps regarding fate and transport in soil and potential impacts on soil clean up…."

Response:

As noted above, DTSC has requested Viscon to submit a technical report that describes Viscon's potential impact on common soil cleanup methods based on the fate and transport test result.

If you have any questions, please contact Li Tang at (916) 322-2505 or at ltang@dtsc.ca.gov.

Linda S. Adams
Secretary for Environmental Protection

State Water Resources Control Board

Division of Water Quality

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Arnold Schwarzenegger
Governor

TO: Stephen d'Esterhazy, CARB

FROM: Robert Hodam, Alternative Fuels Lead, Water Resources Engineer

RE: Response to Peer Reviewer Comments on Fate, Transport, and Toxicity of VISCON in Water and Soil

DATE: Thursday, April 29, 2010

Reviewer Yoren Cohen commented:
"Quantitative information regarding soil infiltration and sorption of PIB (from Viscon or Viscon containing diesel fuel) was not provided. The viscosity of Viscon and diesel fuel containing the Viscon additive formulation will reduce the mobility of these fluid mixtures. Therefore, a specific evaluation of the efficacy soil cleaning methods may be warranted to assess the effect of viscosity as well as viscoelasticity. Another issue that requires attention is the sorption of PIB onto soil particles and the effect of soil organic carbon on such partitioning."

Response:
Given the concentration of PIB in VISCON diesel of 5 ppm, and the relatively small amount of VISCON diesel approved for use in the ARB verification process, the Water Board staff do not feel further research into the impacts of PIB on soil carbon portioning justified.

Reviewer Yoren Cohen commented:
"The spreading of Viscon or Viscon containing diesel on water (e.g., as a result of a spill) is likely to be less than for diesel given the higher shear viscosity and viscoelasticity of these formulations. It is possible that spreading of an oil slick may be also impacted by a change in the surface tension due to the presence of PIB; however, surface tension information was not provided regarding the surface tension of Viscon or CARB diesel containing Viscon."

Response:
According to "Fingas, M.F., D.A. Kyle, N. Laroche, B. Fieldhouse, G. Sergy, and G. Stoodley Publication Year: 1995 Title: The Effectiveness Testing of Oil Spill Treating Agents Source: In: P.Lane (Ed.), The Use of Chemicals in Oil Spill Response, ASTM STP 1252, Philadelphia, PA :286 298" the surface tension of PIB contributes to the containment of oil released into the environment. The SWRCB staff considers containment of oil in the environment a net positive characteristic.

* * *

I generally agree with the conclusions of the other three reviewers on issues related to water quality; aquatic toxicity, fate and transport, and biodegradability.