CONTACT REPORT

February 23, 1959

Company : Socony Mobil Oil Co. Inc.

Location : Paulsboro, New Jersey

Date : February 6, 1959

Report by : M. A. Remondino

Present :

New York		
Mr. E. F. Miller	-	Socony Mobil Oil Co., Inc.
Dr. Samuelson, Med. Dept.		" "
Dr. Arthur Pabst, Med. Dept.		" "
Paulsboro - Product Division		
Dr. J. F. Socolofsky		" "
Mr. D. P. Heath		" "
Mr. R. H. Perry		" "
Mr. W. D. Myers, Jr.		" "
Mr. R. H. Thena		" "
Mr. Harmon F. Hoffman		" "
Mr. Cosmo J. DiPerna		" "
Mr. B. J. Schulz		" "
Mr. Mizelle		" "
Chemical Research		
Dr. John W. Brooks		" "
Dr. Eric J. Y. Scott		" "
Dr. J. J. Giammaria		" "
Others		
Mr. W. W. Hamilton		" "
Mr. Harold Meyers		" "
Safety Engineer at Paulsboro		" "
Several Others		" "
Mr. W. J. Rusher	-	Ethyl Corp. - New York
Dr. R. A. Kehoe		Cincinnati, Ohio
Mr. R. K. Scales		Ethyl Corp. - Detroit
Mr. M. A. Remondino		" "

Tetramethyllead and Alkyl Lead Mixtures

For sometime, the Product Division of the Socony Mobil Laboratories has been working on a problem of severe depreciation by a number of foreign cars of certain fuels marketed in foreign countries. The writer has had numerous meetings, mostly with D. P. Heath, W. D. Myers, Jr., R. H. Perry, and J. F. Socolofsky, concerning this problem and concerning methods for solving it. During these earlier contacts, we were consulted on the possibility of using organic lead compounds lighter than tetraethyllead, with a view to improving the fuel-air mixture distribution in critical foreign cars. In a June 30, 1958 letter to Mr. D. P. Heath, the writer discusses some of the characteristics of tetramethyllead together with precautions for handling. This letter also contained numerous one-page reports which cover certain results from several

earlier programs in our Laboratories. The letter included summaries of effects on engine durability from use of iron pentacarbonyl.

In letters dated August 8 and December 10, 1958 to D. M. Guy, the writer documents other discussions with Socony on this subject. In the December 10 letter, mention is made that in the then not too distant future, the Socony people would want to get together with us for a detailed discussion on the possibility of commercial use of tetramethyllead in foreign countries. There is considerable economic incentive, as outlined in the December 10 letter, to use tetramethyllead in foreign countries.

The meeting scheduled for this date was designed so as to permit Socony to determine what direction to take in the solution of the foreign car fuel depreciation problem. Several routes are open to them, the one with the greatest economic incentive being the use of tetramethyllead. They had been advised on numerous previous occasions that the key to use of TML would be the toxicological and hygienic aspects, and they were anxious to have an opportunity to discuss this with Dr. R. A. Kehoe.

Don Heath acted as Chairman of the meeting. It was mutually agreed that this activity in our two companies be treated confidentially. Mr. Miller stated that he thought that there might be certain patent aspects to their work. We stated that we also thought that there were patentable aspects of our work. Don Heath asked Ray Perry as the first speaker to discuss the technical aspects of the problem. Using slides, Ray showed octane profiles of typical catalytic reformate gasolines presently being made in a number of foreign countries. He then showed the effect of maldistribution of fuel-air mixture to the individual cylinders on the depreciation of reformate-straightrun gasoline blends. Gasoline containing tetraethyllead was depreciated 11.6 octane numbers in the Peugeot 403 French car. Gasoline containing tetramethyllead was depreciated only 6.6 octane numbers. If iron carbonyl is used as the antiknock, the same car will depreciate the gasoline 6.8 octane numbers. MA-250 Mixture (25 mole per cent of the methyl radical) was only about 1/3 as good as tetramethyllead. After surveying a number of American made cars, they bought a standard transmission Ford 6 to test with the French Peugeot. The Ford 6 does not depreciate the fuels quite as much as the Peugeot, but directionally, it treats foreign gasolines much like the Peugeot.

Perry pointed out that as the lead concentration in the gasoline is increased, the superiority of tetramethyllead over tetraethyllead is increased.

Socony have found that the knocking problem occurs at low speed, generally below 1500 rpm and that gasolines such as they would like to make in foreign countries (blends of catalytic reformate and straightrun) are much worse than blends of cat-cracked and straightrun.

Their studies indicate that based on actual engine performance, the antiknock benefits from use of tetramethyllead are greater than would be calculated from the lead concentration of the whole fuel. Their calculations are based on correlations involving the volume fraction of the IBP-220° cut and the Research octane number of this cut. Based on the road performance, the lead concentration of the front-end cut appears to be higher than that of the whole fuel.

It is known that in addition to testing iron pentacarbonyl in this program, they have also conducted numerous tests on ferocene. We were furnished an extensive tabulation of road depreciation data in quite a number of European cars. These tests were conducted in England, France, Germany and Italy. They also furnished a table showing gasoline and TEL usage. Ray Perry estimated that the four countries, France, Germany, Italy and UK (this represents about two-thirds of the European market) consume about 97 million barrels per year of regular grade gasoline and 50 million barrels per year of premium. This corresponds to a 66, 34 ratio. He estimated that these four countries used 31 million pounds of lead as TEL in 1958.

A copy of the tables and charts corresponding to the slides used by Ray Perry are in the files of the writer.

Don Heath then discussed some of the other problems of interest. He emphasized that there is much greater demand for middle distillates and intermediates than there is for gasoline in the foreign markets. They are now making 20% of the barrel into gasoline, and they would very much like to reduce this percentage. It is obvious that in addition to the increased road antiknock performance from TML additional economic benefits would accrue through a reduction in the amount of gasoline manufactured from a barrel of crude. Heath also pointed out there was a currency problem involved. As time goes on, they are finding it more difficult to get dollars for buying materials from outside of these European countries. He stated that if the TML program were developed to commercialization, it would be necessary eventually to manufacture TML or other lead alkyls somewhere in the Common European Market. This is due strictly to the currency problems.

A sample of the MA-750 mixture had been sent to Paulsboro, but they had not had an opportunity to test it. Road Antiknock performance tests on this material will be conducted as soon as they can be scheduled. Because of the rather disappointing performance of MA-250, the Socony research people are hoping that TML could be used commercially. Although they have been discouraged (or rather they have not been encouraged) frequently on the prospects of TML ever becoming commercial, they wanted to be sure there was no possibility of using TML before taking another avenue of approach to the solution of the problem.

At this point in the meeting, it was thought that since the Medical aspects of the use of lighter lead alkyls were the key to commercialization of any of them, Dr. Kehoe was called upon to discuss the over-all medical side of the use of lead in gasoline.

Dr. Kehoe discussed rather briefly the background concerning the successful use of tetraethyllead in gasoline. He emphasized that the development of the precautionary measures in the manufacture of TEL and handling of leaded gasoline have been supported by more than 30 years of experience. The handling of lead either in the manufacture or in the gasoline, causes little concern when the material is in the hands of the lead manufacturers or the petroleum industry. This is because the industries require close adherence to the special precautions developed years ago. Greatest cause of concern with TML would be one where people outside of industries would be handling gasoline containing lead. Examples are: filling gasoline tanks at service stations, having open containers of gasolines, carburetor repair areas in garages, gasoline spillage, etc.

It has been shown that lead in gasoline does not contribute to air pollution. It was Dr. Kehoe's opinion that alkyl lead compounds lighter than tetraethyl would not contribute to air pollution.

Possible problems from use of more volatile lead compounds in gasoline at retail level are of two types. First, inhalation of vapor containing lead and secondly, contact with the skin.

Dr. Kehoe cited several cases of lead intoxication with TEL during the war. Cases were found in England, Egypt and Iran where personnel were filling blitz cans in completely closed areas without ventilation, (this was because of blackout restrictions). He mentioned another case where cans of gasoline were stored underground on the island Malta. The bottom cans had been crushed and were leaking badly. In the blitz can filling operations and the Malta underground storage, the lead concentration in air was found to be as high as 30 mg per cubic meter.

He cited another case during the war whereby someone in England had set up a clothes cleaning operation using leaded aviation gasoline. In this case, the operators of steam clothes presses received lethal doses of TEL in the closed room when pressing clothes that were not dry after the cleaning with aviation gasoline.

Dr. Kehoe cited results from experiments conducted at the Kettering Laboratories as follows: If 1 cc of concentrated tetraethyllead is rubbed on the belly of a rabbit and allowed to absorb for two hours, then it is cleaned off, rabbits will die within 48 to 72 hours. In the case of TML, it was impossible to give a rabbit a lethal dose by skin absorption. It was found that approximately 35 mg. of elemental lead per kilo of body weight is fatal to rabbits in this type of experiment.

So far as skin absorption is concerned, a concentration of lead in gasoline of 1 part in 10 is considered lethal. At a concentration of 1 part in 100, absorption will take place, but it is not considered lethal. The limit in this case being dependent upon how much gasoline can be put on the skin, before a serious rash develops. At a concentration of 1 part in 1000, absorption is negligible. Dr. Kehoe stated that it looks like 6 cc's of lead per gallon is about as high as can be considered safe from the standpoint of skin absorption.

So far as volatilization of lead with gasoline is concerned, the lead content in the vapor follows Rault's law. This has been demonstrated by experiments. Air saturated with TEL at a temperature of 25°C is lethal in 15 minutes. This corresponds to a concentration of 5 mg of lead per liter of air. Dr. Kehoe thought that with tetramethyllead, the vapor factor is the important point. Lead-in-air with tetramethyllead is about 100 times that with tetraethyllead. Under ambient conditions, tetramethyllead would be expected to volatilize with gasoline at a faster rate than tetraethyllead, hence it is thought that tetramethyllead in gasoline would not be absorbed through the skin as much as will tetraethyllead.

Dr. Kehoe stated that in many cases, more lead gets into the atmosphere from other sources than from use of tetraethyllead in gasoline. He cited for example that in Cincinnati the burning of coal contributes more lead in the atmosphere than tetraethyllead. He further stated that when you burn any

natural material, such as coal, wood, etc., you put lead in the air. Even though TML has a higher vapor pressure than TEL, he did not think that the lead content of the air in cities would be increased by the use of TML in gasoline.

Dr. Kehoe stated that at the present time and in theabsence of extensive tests with tetramethyllead, it could not be substituted directly for tetraethyllead without investigation. Concerning the mixtures he would not want to go to MA-750 or even MA-500 without conducting some tests. Dr. Kehoe suggested that they look at mixed alkyls since he thinks that TML could not be used.

The meeting was next opened for questions and most of these concerned the medical aspects. Some of the questions asked of Dr. Kehoe follow.

Question: John Payne, when you breathe TEL vapor, do you exhale some of it?

Answer: Yes, you do. The amount exhaled can be calculated, and it is proportional to the partial pressure.

Question: In the analysis for lead in body excretion, can you separate the organic from inorganic compounds?

Answer: In analyzing excretion for lead, the lead compounds are reduced or otherwise changed so that the organic portion is destroyed for the analysis. In other words, all of the lead compounds are converted to the inorganic form for analysis.

Question: Is methyllead perse more toxic than ethyllead, or is it just a problem of higher volatility?

Answer: TML is less toxic and Dr. Kehoe guessed that TML probably decomposed more easily in the tissues and thus more easily excreted.

Question: Is there more lead in vapor with TML in the first 10% off of gasoline?

Answer: Yes, because of its volatility.

Question: What about tank cleanings with TML?

Answer: Couldn't guess the answer to this. In elaborating on this answer, Dr. Kehoe stated that TEL can be found in tank sludge. There are two known ways in which this can occur. First, if concentrated tetraethyllead is added to a tank containing gasoline, without proper agitation, the tetraethyllead being heavier will go to the bottom. On raching the bottom, it will eventually go under the water layer and remain there as tetraethyllead. A second way, is that the decomposition products of tetraethyllead can revert back to tetraethyllead as long as there is some of the organic portion present. This will not happen when all of the decomposed lead is inorganic.

Question: How much money has been spent on the medical aspects of use of TEL in gasoline?

Answer: Several million dollars (my notes indicate 1.5 to 2.0 millions of dollars).

Question: What expenditure would be required on tetramethyllead?

Answer: About the same, but over a period of years to follow its use.

Question: Would Dr. Kehoe consider use of MA-250 as satisfactory for direct substitution with TEL?

Answer: It might be feasible, but would have to be investigated.

Question: E. F. Miller, what is the basis for Dr. Kehoe's opinion about the use of tetramethyllead, is it based on extrapolation from TEL to TML, or is it from experience?

Answer: It is all based on extrapolation..

Question: W. D. Myers, how would you assess problems from use of TML or how would you visualize the problem?

Answer: Must use experimental observations with tetramethyllead.

Question: D. P. Heath, what is the next step that must be taken on this entire problem and what does it take to make the next step?

Answer: We must look at high hazard areas, such as gasoline loading racks, carburetor overhaul areas, service stations, etc.

Question: If Socony is interested, what is the next immediate step?

Answer: Try some experiments on a very small scale in the laboratory, simulating operation with lead-in-air. If this passes, the next step would be to an actual miniature operation with lead-in-air (loading racks, service stations, etc.) so that the effect on humans can be studied. In elaborating on this answer, Dr. Kehoe had the following to offer: .75 mg of PB per cubic meter of air is the maximum concentration except for a fleeting period. .2 mg per cubic meter of respirable lead is the maximum allowable limit for an 8-hour day, 5 days per week occupation. This is with medical supervision. This is the threshold value of lead in the lead trades. Air in the country now contains 3 to 5 micrograms of PB per cubic meter with much of it now being only 2 micrograms. City air, in Philadelphia for example, contains 5 to 9 micrograms per cubic meter.

Question: What is the relative danger of inhaling TML compared with TEL?

Answer: The inhalation of TML is appreciably less dangerous than TEL (more TML would be exhaled).

Question: How do you measure the effect on humans?

Answer: The effect is measured on the basis of excretion of lead by the body. For example, inhalation of lead at a concentration of 15 mg per cubic meter will show up in the urine in 48 hours.

Question: What would be a negative result, or in other words, a safe level of operation based on lead in the urine?

Answer: If there is no change in excretion of lead by personnel in two months time he would consider it okay.

Question: B. J. Schulz, if a program on TML were undertaken, how long would the medical test take and how much would it cost?

Answer: Dr. Kehoe estimated the cost would be about $100,000 so far as Ethyl is concerned, and this would include work at the Kettering Laboratory. So far as time is concerned, they would want to watch men for several months. If no trouble shows up, in several months, it might be possible to get contingent approval from the Surgeon General. This would mean permission would be granted contingent upon close medical supervision.

Question: When would the Public Health Service have to be approached on such a program?

Answer: We don't have to take the program to the Public Health Service while the experiments on the miniature operation are going on. It will be necessary to take the matter to the Public Health Service before these materials are used commercially.

Question: Would it be necessary to take this to the Public Health Service if the materials are going to be used abroad?

Answer: The first question that would be asked by medical people abroad is, "Did the U. S. Public Health Service approve this?" It would probably be difficult to get medical approval in foreign countries, if the U. S. Public's Health Service does not approve.

Question: E. F. Miller, if a program on TML or the lead alkyls were to be undertaken, what would Ethyl contribute to such a cooperative test?

Answer: It would be a cooperative program in which Ethyl would handle the tests and analyses so far as the medical aspects are concerned. The second step in the program, i.e. the small scale gasoline handling operation such as loading racks, service stations, etc. would have to be done some place on Socony property since Ethyl has no properties of this kind. Dr. Kehoe says that they at the Kettering Laboratories would want to be involved in the medical work. Moreover, the Kettering Laboratories has the equipment, procedures and men to do it.

Question: Mr. Miller asked if Ethyl would care to consider the hygienic problem an industry problem for those companies marketing or the countries being considered.

Answer: We did not believe that this was desirable at this time, because it was felt that the experimental program should be kept as small as possible.

There was not time to cover other phases of this broad subject even though the writer had information with him. It was thought advisable to leave the material with Socony so that our data could be considered in planning future programs. The following material was left with Mr. Heath.

1. A write-up "Evaporation of Lead Alkyls" by H. J. Gibson. This based on recent analyses for lead-in-air in drum experiments and in the Ethyl garages at Detroit and San Bernardino.

2. The write-up of "Evaporation of Lead Alkyls" by H. A. Beatty. Summary of previous experiments on this subject.

3. Table summarizing the laboratory and road antiknock effectiveness of lead alkyls. Road performance obtained in Cadillac and Pontiac passenger cars.

4. Curves showing octane-temperature profiles of several base fuels used in the road and laboratory antiknock effectiveness programs.

5. "Laboratory Antiknock Evaluation of TML, MA-250, MA-500, MA-750 and TEL in Finished Gasolines". This is a Refinery Technology report dated January 15, 1959.

The Socony people expect to study the information obtained during the meeting, then they plan to hold a company meeting to determine the next step in this program. We will be advised of their decision. Ed Miller will advise us of their estimates of demand based on the cost estimates which we supplied them.

Don Heath and Walt Myers offered us quantities of their two reference fuel systems which they use for gaging the extent of the depreciation problem in foreign cars. As an alternative, they offered to road rate in their Peugeot and Ford 6 the base fuel systems we are using in our studies of TML and the alkyl-lead mixtures. This would appear to be a good opportunity to get a tie-in between the antiknock performance in U. S. cars and foreign cars.

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