C O N F I D E N T I A L

ETHYL CORPORATION

Chemical Research Laboratory

To: Members of Research Committee

From: George Calingaert Address: Detroit

Subject: Iron Carbonyl Date: March 4, 1944

The possibility of commercial use of Iron Carbonyl as an antiknock agent has in the recent past received a great deal of attention from our Research Laboratories, and several of the problems involved in such a development have been presented at meetings of the Research Committee and of the Coordination Committee, sometimes briefly and sometimes more thoroughly. There seems however to be no written presentation of the subject as a whole. The present memorandum attempts to list, describe briefly, and evaluate as well as possible, the individual subjects which, taken together, constitute the whole picture. It is hoped that, having before us this summary, possibly amended and supplemented, we will have a clearer understanding of the problems facing us, and will be in a better position to advise the Management of our estimate of the situation and our recommendations for a future course of action.

Broadly stated, and after narrowing down by preliminary work, the field as it now stands is that of marketing as an antiknock material a mixture of tetraethyllead and iron carbonyl, in the ratio of 1:3 by volume, and to be used in concentrations not to exceed 0.5 cc. TEL and 1.5 cc. of iron carbonyl per gallon. The whole field can be divided under the eight following headings, which are discussed below:

I. Procurement
II. Engine Performance
III. Health Hazards
IV. Stability
V. Ignition Difficulties
VI. Engine Wear
VII. Wear-Reducing Additives
VIII. Procurement of Additives

I. Procurement

Tetraethyllead is available commercially. Iron Carbonyl is a known compound; the raw materials for its production are cheap and plentiful, and the manufacturing process is well known and has been successfully used on full industrial scale. A study of the patent situation has revealed no dominating patents which would prevent us from entering the field. Some patents which may be of interest as

KE 0003321

improvements are now controlled by the Alien Property Custodian, and licenses could be obtained at a nominal charge. However, the exact details of a manufacturing process will have to depend on the result of experimental work of our own. Such an experimental project was started in the Chemical Research Laboratory over a year ago, but was interrupted a few months later; active work will be resumed in a fe weeks.

II. Engine Performance

This has been studied exhaustively by the Engineering Labor The performance of the material in modern engines makes it unusually attractive, both by comparison with present-day fuels, and on a pri basis, even when the calculation is based on the most conservative estimates of its manufacturing cost. The economic picture may be ma less favorable by the necessity, discussed below, of using additives the cost of which cannot be even guessed at this stage. If, as it i hoped, the cost of additives is not prohibitive, the use of the prod will depend solely on the satisfactory solution of the technical pro described below.

III. Health Hazards

The latest reports from the Medical Department are to the that the material is intrinsically less toxic than tetraethyllead. view of its greater volatility, however, protection against direct e posure to the vapor of concentrated iron carbonyl is indispensable. would probably be well at this point to take the matter up again wit Medical Department for final confirmation of the previous reports, for consideration of a further experimental program on the subject.

IV. Stability

The factors affecting stability are: air, heat, and light. tetraethyllead component of the new fluid is known to be sufficientl stable to withstand normal exposure to these factors. Iron carbonyl known to be stable to heat, and there is no indication that it is no also stable to normal exposure to air, provided light exposure is ex cluded. The compound is, however, unstable to light. Several sta- bilizers have been described, mostly in the patent literature. A ra extensive re-survey of the field recently completed by the Chemical Research Laboratory showed that these are not wholly effective, but f to uncover any new or better stabilizers. It is a fair estimate at stage that air and heat stability are adequate, but that exposure t light must be minimized, or else serious difficulties may result.

V. Ignition Difficulties

In the early use of iron carbonyl, spark plug failures constituted one of the two major drawbacks of the product. This trouble has been considerably decreased by lowering the concentration at which iron carbonyl is used, but not, however, to the vanishing point. Comparatively little information is available on the effect of corrective agents, primarily (as noted below) because of the unavailability of compounds having the necessary physical properties for use in an engine. What data have been obtained suggest that the problem is still a sizeable one, although probably not as critical as the wear problem.

VI. Engine Wear

The greatest obstacle to the use of iron carbonyl is its effect on engine wear. Comprehensive data are available which indicate, by and large, an engine wear five times that obtained on present-day ETHYL gasoline. As in the older case of the use of bromine compounds for the removal of lead from the engine, there is every evidence that the effect of any fuel additive will be due to the elements added, and not to the type of compound in which form the elements are present. The evidence on the specific effect of the elements is rather extensive, and points to only five elements as being available at a reasonable price and having appreciable wear-reducing characteristics. These five elements are: zinc, copper, titanium, calcium, and barium. In the most favorable tests the wear was reduced down to 200% of normal. Some evaluation is needed at this point of how much greater wear than normal, if any, can be tolerated. It seems highly probable that cost alone does not govern here. Cost-conscious fleet operators may tolerate additional wear if they can be satisfied that this is more than offset by other decreases in cost, but competitive advertising alone would keep private owners from using any fuel causing perceptible trouble. Perhaps the only criterion then will be: by how much can the wear increase before it becomes noticeable. An evaluation of this factor is necessary for a correct appraisal of our present position on the wear problem.

VII. Wear-Reducing Additives

Quite distinct from the question of: which element is desirable in an additive? is the question: what are the necessary characteristics for a marketable fuel additive?

Our extended experience in the present investigation as well as in the marketing of ETHYL Fluid enables us to set down minimum specifications for any material which is to be marketed as a gasoline additive. These specifications are:

KE 0003323

1. It must be a liquid, at least down to 32°F., and if it contains any solid components, these should be present in very small amounts only, such as dye in ETHYL Fluid.

2. It must be gasoline-soluble, preferably miscible in all proportions, or at least soluble down to -10°F. in concentrations several times that normally used. This should be true solubility, not dispersion, such as an emulsion, and should not require the use of a third mutual solvent, the effect of which might be lost on dilution.

3. It must be stable to water and insoluble in it, or nearly so, because otherwise it would be extracted when the gasoline is in contact with water, in storage tanks, in settling bowls, etc.

4. It must be completely stable to air at ordinary atmospheric temperatures.

5. It must have "Inductibility into the combustion chamber". This new term refers to the ability of the material to be successfully transported from the carburetor jet into the combustion chamber, and it depends simultaneously on several physical properties.

   One of the necessary properties, already discussed above, is that of being liquid. Experience has shown that solids will deposit in some types of intake manifolds through which liquids might be entrained. The other two properties are: volatility, and stability to air under the conditions existing in the intake manifold. The specifications on these two properties are interrelated: a very volatile material need not be very stable, because it will remain in the manifold only a short time, and have little contact with the hottest walls of the manifold. A non-volatile liquid will to some extent deposit on the walls and will depend for its induction on being swept in by the charge; its prolonged contact with hot surfaces therefore will call for a much higher degree of stability. Here are a few illustrations: tetraethyllead is equally successfully introduced into the combustion chamber through a hot or cold manifold, even though it is known that the compound would be quickly oxidized if kept at the temperature of the hotter wall of the manifold. Top lubricants, even some consisting of rather heavy but stable lubricating oil, can be used successfully, most likely because while they are not volatile they are stable enough to withstand the wall temperature of the manifold and are swept into the combustion chamber by the charge. On the other hand, some zinc compounds which are liquid, but have neither the volatility of tetraethyllead nor the oxidation stability of lubricating oil, leave heavy deposits in the induction system.

Bearing in mind the range of conditions in intake manifolds, the following tentative specifications are offered:

(a) A vapor pressure of at least 1 mm. at 50°C., with not more than 5% decomposition by air-bubbling for 5 minutes at 100°C., or:

(b) With a vapor pressure less than 0.1 mm. at 50°C., not more than 5% decomposition by air-bubbling for 5 minutes at 200°C.

VIII. Procurement of Additives

In the course of this investigation, a large number of compounds of many elements have been prepared by the Chemical Research Laboratory, and considerable information has been accumulated, both from the literature and from our own work, regarding the physical and chemical properties of these compounds. So far, no compound of barium or calcium has been found which begins to approach the minimum specifications; as regards the other three desirable elements, titanium, copper, and zinc, volatility is often available at the expense of stability, and the most stable of the gasoline-soluble liquid compounds show insufficient volatility, while their stability still falls far short of that of lubricating oils. The whole field is being reanalyzed at this time with all the available expert talent, and a statemant on the subject will be available in the near future.

IX. Conclusions

Subject to such corrections and additions as may be offered by other members of the technical staff of the Corporation, the present status of the marketability of iron carbonyl may be summarized as follows:

A. No Problems

The Procurement and Antiknock Effectiveness leave no special problems the outcome of which is at all doubtful.

B. Minor Problems

The Health Hazards are probably not excessive; the exact status of the problem could be ascertained readily from the Medical Department.

The Stability may or may not constitute a serious problem, depending on an evaluation of the amount of light exposure to be expected under normal conditions.

C. Major Problems

Ignition Difficulties and Engine Wear loom as two serious problems. Both appear to be still in the stage where trouble is greater than normal. It would be interesting at this stage to have estimates of:

(a) How much above normal are the wear and ignition trouble observed when the best additives are used;

(b) How reliable is the estimate of (a);

(c) How likely it is that further work will improve estimate (a).

Procurement of Wear Additives. - A statement will be available shortly regarding:

(a) How certain are we that the specifications now set for a satisfactory additive are correct;

(b) What is the likelihood of preparing a satisfactory additive;

(c) What is the reliability of estimate (b).

It is the hope of the writer that a careful consideration of the above material by all the interested members of our technical staff will lead to an intelligent evaluation of the status of the problem as a whole, so that in turn the best decisions can be made as to the proper orientation and intensity of our research activity in this field.

George Calingaert

George Calingaert

C:M

Copies to: E. W. Webb
T. Midgley, Jr.
R. A. Kehoe