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Stability of "Ethyl" Antiknock Compound — November 21, 1947

Enclosed are three copies of memorandum on "Stability of "Ethyl" Antiknock Compound".

The report was written with the view of presenting information relative to the stability of our product in a manner easily understood by safety engineers and other field representatives.

The first draft of this report was reviewed by Drs. Calingaert and Beatty and other members of the Chemical Laboratory. Their additions and corrections were integrated in the final report.

It is deemed desirable that this report should receive general distribution in the field since it contains information of interest to all who deal in the distribution of our product.

The reader of this report should be cautioned in its use since it contains information of a restricted nature. This is especially true for the information contained in the section dealing with the use of inhibitors for the stabilization of fluid.

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ETHYL CORPORATION
Research Laboratories
Detroit, Michigan

November 20, 1947

Stability of "Ethyl" Antiknock Compound

Stability of "Ethyl" fluid has been traditionally considered as the problem of the Chemist. This is as it should be. However, a considerable amount of information has been collected on this subject which profitably should be in the hands of the field personnel.

It is not uncommon for our field people to be confronted with questions concerning the deposition of sludge in tanks, drums and in other facilities used for the storage of fluid. The reasons for the presence of this sludge are probably not too well understood. Hence it seems desirable that appropriate information on fluid stability be passed on to those who deal in the distribution of our product.

It is the purpose of this report, therefore, to present the results of recent laboratory investigations dealing with the factors of fluid stability, to discuss the use of inhibitors for the stabilization of "Ethyl" fluid, and to interpret the laboratory data for field application.

General Considerations

Description of Compounds

Before proceeding to a consideration of the factors of fluid stability, it may be well first to review the properties of the chemical compounds involved, especially those which comprise sludge.

As you will recall, tetraethyllead is an organic molecule, that is, the lead atom is attached to carbon atoms. The molecule is composed of one atom of lead attached to four ethyl groups.

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 H H
HC-C-  represents an ethyl or "Et"
 H H
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group. For purposes of this report, molecular tetraethyllead is written as follows:

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   Et
   |
Et-Pb-Et
   |
   Et
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When we speak of organic lead salts, we mean, in general, the successive replacement of the ethyl groups by other groups, such as chlorine or bromine. Examples of organic lead salts are triethyllead chloride, diethyllead dibromide, etc. The molecule is considered to be organic in nature until all the ethyl groups have been replaced by other groups, at which time the molecule is said to be inorganic in nature. Examples of inorganic compounds of lead are: lead bromide ($PbBr_2$), lead chloride ($PbCl_2$), lead sulfate ($PbSO_4$), and lead oxide (PbO).

Since organic lead salts are the more important compounds associated with fluid sludge, and yet least understood by the non-chemist, a description of these compounds is given in detail.

Triethyllead halides (Et_3PbX) are colorless solids at room temperature. Triethyllead chloride decomposes when heated to about 120° C. (248° F.). Triethyllead bromide melts at 103° C. (217° F.), with decomposition, to a turbid liquid. Triethyllead halides in the form of dust are exceedingly irritating to the nasal membranes when breathed; they cause excessive sneezing. If they are breathed for a prolonged period, they produce a severe headache.

A very important property of triethyllead compounds is that they undergo a type of decomposition reaction to produce tetraethyllead. This takes place quite rapidly at elevated temperatures, for example during steam distillation, and also occurs slowly at room temperature. This property of the compounds needs to be seriously considered whenever fluid sludge is handled in any manner.

Information regarding the solubility of these compounds in different solvents is important. With the exception of gasoline, triethyllead halides are very soluble in nearly all organic liquids, including tetraethyllead. Triethyllead bromide is soluble to the extent of 50% by weight in "Ethyl" Motor Mix; triethyllead chloride, to the extent of 5% by weight in "Ethyl" Motor Mix. Hence, it is to be noted that fluid decomposition products, such as the triethyllead halides, will tend to dissolve in the fluid and not appear as deposited sludge.

Triethyllead hydroxide (Et_3PbOH) is insoluble in "Ethyl" brand of antiknock compound and gasoline, but fairly soluble in water.

The other organic lead (dialkyllead salts) and inorganic lead salts are practically insoluble in antiknock fluid. As a result, when they are formed as deterioration products of the fluid, they will immediately come out of solution, and deposit on the bottom or sides of the container. These salts when pure are colorless, but their deterioration on standing in the presence of traces of air or water yields yellow and brown oxides of lead, so that most of the sludges observed are colored.

Composition of "Fluid" Sludge

Generally speaking, the term "sludge" designates decomposition products which settle to the bottom or sides of the container. The term "sludge" as used in the Laboratories of this Corporation, however, means decomposition products which are soluble in the fluid or potential sludge as well as the decomposition products which precipitate. In substance then, by the term "sludge" as used in this report is meant both potential sludge and precipitated sludge.

Although the exact composition of fluid sludge will depend on various conditions (such as composition of fluid, temperature, exposure to air, etc.), in general, precipitated sludge is composed of inorganic lead compounds, such as lead bromide, lead chloride, lead oxides, bismuth oxides; and organic lead compounds, such as diethyllead dichloride and dibromide, and various oxides of these compounds.

Elementary analysis of typical precipitated sludges obtained from commercial fluid (recent) in the laboratory is given:

	Analysis of Precipitated Sludge		
	% Lead	% Bromine	% Chlorine
Motor Mix	58.6	7.72	0.0
Aviation Mix	59.8	7.96	-

To present a further picture of the composition of precipitated sludge, the following table gives analysis of sludge removed from a refinery weigh tank for "Ethyl" Antiknock Compound:

Compound	Analysis of Weigh Tank Sludge % by weight
Organic lead salts	27
Inorganic lead salts	19
Bismuth compounds	39
Ferric hydroxide	15

It is to be noted that this sample of sludge was obtained from a tank which had been in operation from 1931 to 1944 and hence had a high bismuth content for the reason explained below. The ferric hydroxide content, of course, is rust from the tank.

The potential sludge of "Ethyl" fluid is composed mainly of triethyllead bromide and triethyllead chloride. In due time these compounds become oxidized by the atmosphere and precipitate as sludge.

In small amounts dissolved sludge is considered to have no deleterious effect on the storage of fluid. However, a fluid containing a relatively large amount of potential sludge is not desirable since when it is dissolved in gasoline the triethyllead salts will precipitate due to their limited solubility in that medium.

The disadvantages of precipitated sludge are obvious. The sludge may build up in drums, weigh tanks, lines, etc. and consequently increase the handling and distribution problems of the fluid.

Storage Stability of "Ethyl" Fluid

Stability of Fluid Prior to 1940

Prior to about June, 1940 it was generally noted that a considerable amount of sludge had deposited from "Ethyl" antiknock fluid into drums and tank cars. This condition was a source of considerable annoyance to the Corporation and to its customers. Research work in our Chemical Laboratory and subsequent development by the Ethyl and duPont manufacturing groups provided a means of eliminating the ready sludge-forming materials from tetraethyllead before it was blended to "Ethyl" fluid. This came about in the following way.

At the time analysis of sludge obtained from the fluid invariably showed high bismuth content. Consequently, it was thought that the bismuth compounds in the tetraethyllead were largely responsible for the excessive sludge formation. Laboratory investigations revealed that this was true.

It was found that commercial lead which was being used in the manufacture of tetraethyllead contained a small percentage of metallic bismuth. In the reaction for the formation of TEL, the bismuth in the alloy would also react and form a compound triethylbismuth, similar to TEL. This compound in the laboratory was noted to be highly unstable and easily oxidized by air to form compounds which would deposit from the fluid.

Laboratory studies showed that TEL could be freed of this compound merely by blowing air through TEL before it was blended into fluid. This procedure was incorporated by the Manufacturing Department. As a result, the sludge at that time in crude TEL was greatly reduced, from 0.2-0.3 g. of precipitated sludge/100 cc. TEL to 0.01 g. sludge/100 cc. TEL, and was later reduced still further, to 0.002 g./100 cc. TEL. This has resulted in the elimination, for all practical purposes, of the difficulties with sludge settling out in relatively large amounts in blender, bulk storage tanks, drums and tank cars under normal storage conditions.

Stability of Current Fluid and the Factors Affecting its Stability

As a result of the increased purity of TEL, the sludge problem of "Ethyl" antiknock fluid was greatly diminished. Current commercial fluid contains only a trace of deposited sludge. On blending the fluid or shortly thereafter, a trace of potential sludge is formed by reaction of the TEL with the ethylene dibromide or impurities therein, but this amounts to less than 0.3% of the TEL content, and under proper storage conditions the reaction comes to a halt.

Although our manufactured product, as delivered to the customer, is almost entirely without sludge, under certain conditions of storage "Ethyl" fluid will "age" with consequent formation of a slight amount of sludge. The factors which affect the storage stability of "Ethyl" antiknock fluid are discussed in the following sections.

1. Effect of Oxygen or Air. - Laboratory studies and field experience show that when "Ethyl" fluid is exposed to air deterioration of the fluid occurs. The air is dissolved by the fluid, slowly on standing and rapidly when the fluid is agitated. At room temperature "Ethyl" fluid can dissolve 10% of air by volume.

The sludging reactions of fluid in the presence of air occur in two stages: first, a fast oxidation reaction producing a soluble lead sludge, presumably an alkyllead oxide; second, by a reaction between this compound and ethylene dibromide (a constitutent of fluid) to form triethyllead bromide. The latter compound constitutes potential sludge, if the amount of available air is limited. If the amount of air is unlimited, the potential sludge is converted to decomposition products which are insoluble in the fluid and settle to the bottom of the container. In this connection, laboratory studies have shown that there will be several times as much potential sludge as precipitated sludge.

In a typical experiment "Ethyl" Motor Mix on standing at room temperature over a period of seven days in a sealed quart jar with a large but limited air space gave 0.16% (weight % TEL) as precipitated sludge. In similar experiments and under the same conditions it was found that fluid in open quart jars gave about 50 times as much precipitated sludge as fluid in sealed jars.

With all other variables constant, therefore, in general, it can be stated that the extent of fluid decomposition will depend on the amount of air available.

2. Effect of Time and Temperature. - In order to determine the effects of time and temperature on fluid stability, laboratory tests were run in quart bottles for periods up to 28 days and temperatures ranging from 50° to 95° F. In the tests where an unlimited amount of air was available, it was found that sludge formation (precipitated sludge) increases with increasing time and temperature. In these tests it was also concluded that where air is not available the increased temperature merely served to accelerate the rate of approach to a constant sludge level.

The effect of time and temperature on fluid stability have been demonstrated in drum storage tests also. In one test, a drum of fluid (Motor Mix) was stored for 96 days at a constant temperature of 140° F. Inspection and analysis of the fluid after the test showed that the decomposition of the fluid to soluble sludge increased slowly to the extent of 0.3% of the TEL, and that there was very little precipitated sludge. In this test, incidentally, the pressure of the drum rose initially to a maximum of 19 pounds gage; within one day the air in the drum (3%) dissolved in the fluid, the drum became shell-full, and the pressure fell to 8 pounds where it remained constant for the duration of the test.

In summary, the factors of time and temperature (up to 60° C. (140° F.)) contribute very little to sludging of fluid, if the fluid is in closed containers and consequently exposed to only a very small amount of air. Conversely, they contribute greatly to fluid sludging if the fluid is being exposed to an unlimited source of air.

3. Effect of Light: - The exposure of fluid to light in any form increases sludge formation.

In a representative series of laboratory experiments, 234 ml.-samples of fluid, protected by a water layer, were stored in pint bottles and exposed to daylight and darkness for a period up to 20 months. At the end of this storage period, the fluid sample contained a 1/8-inch layer of sediment (precipitated sludge), yellow crystals of material formed on the sides of the bottle, and there was a brownish frosting of the glass above the fluid. The samples exposed to daylight gave 0.9 gram of precipitated sludge, while the samples stored in the dark gave 0.3 gram of precipitated sludge. Thus, in this case at least, daylight exposure of the fluid gave a three-fold increase in sludge formation over the samples stored in the dark.

At the present time "Ethyl" antiknock fluid is being handled and distributed in opaque containers; and as a result, there is very little chance for exposure of the fluid to light. There is, however, some light exposure of small quantities of fluid used in gasoline laboratories for testing purposes.

<u>Protection of "Ethyl" Fluid Against Deterioration by use of Inhibitors</u>

Although "Ethyl" Fluid is relatively stable under ordinary storage conditions with only trace formation of sludge, the Corporation has and is giving much consideration to the problem of finding a suitable inhibitor for "Ethyl" antiknock fluid. A completely stabilized fluid is considered advantageous both from the economic and safety standpoint. Such a fluid would eliminate all distribution problems from the standpoint of sludging in the containers, and would minimize the handling of lead sludges in cleaning gasoline storage tanks and fluid bulk storage tanks.

Of the many inhibitors which have been tested in the laboratory for the stabilization of fluid, Shell 24M6B (2,4-dimethyl-6-tertiary butyl phenol) has proved to be one of the most effective. Laboratory investigations have demonstrated conclusively that inhibitor 24M6B at a concentration of 0.1% (based on weight of TEL) in "Ethyl" fluid considerably decreases the amount of sludge formed when the fluid is exposed to air. The use of the inhibitor in this concentration gave satisfactory protection of "Ethyl" antiknock fluid for three weeks at 40° C. and for one week at 50° C. The reason the inhibitor does not give unlimited protection is that the inhibitor itself is used up in time.

Shell 24M6B inhibitor has been put on the list of satisfactory inhibitors for use in the stabilization of "Ethyl" antiknock compound. However, at present it is being used in special cases only. Regarding its use in commercial fluid, a careful study of the subject made by the Corporation showed that there was no need for a stabilizer under our normal bulk handling of the fluid. In addition, it was felt that since the inhibitor cannot eliminate sludging <u>completely</u>, its use cannot be justified.

The inhibitor is currently being used to stabilize fluid shipped in one-liter cans. The use of canned fluid, you will recall, involves the use of fluid in the laboratory under conditions where it is highly exposed to air. Opened and partially used cans of fluid are subject to long periods of storage with intermittent exposure to air upon opening the can to remove a small portion of the fluid. Without inhibitor this exposure resulted in fluid burettes becoming coated with a deposit difficult to clean, and the fluid itself became hazy.

In order to eliminate or minimize these sludging reactions Ethyl Corporation is supplying "Ethyl" antiknock fluid (Aviation) in a dilute form (solvent is 70% xylene + 30% <u>n</u>-heptane by volume) and stabilized with 0.1% 24M6B, as a service to our customers. Laboratory tests have shown that the inhibited canned fluid is satisfactorily stable for use during periods up to six months.

<u>Application of Fluid Stability Data to Field Use</u>

In order to supply our customer companies fluid with the least amount of deterioration, consideration of the following precautions in the field is suggested:

Weigh Tank Storage

Our present system of storing fluid in customer refineries in weigh tanks is advantageous since it does not allow exposure of the fluid to light at any time.

Glycerine is added to fluid in weigh tanks for the purpose of forming a protective blanket. The glycerine, being insoluble in the fluid and having a density lower than the fluid, will form a separate layer on top of the fluid. By means of this layer (blanket) contact of the bulk fluid with air is largely guarded against and the tendency of the fluid vapors to escape is greatly decreased. It cannot be emphasized too strongly, therefore, that all weigh tanks should contain a glycerine blanket, if space in the tank is available for it. Without a blanket, deterioration of the fluid can be expected to increase, especially if the vent line has to be left open.

In the operation of a mixing plant, there exists the possibility of pulling air through the fluid, which should not be permitted. This may happen when the supply of fluid in the tank is low, at which time air is sucked through the standpipe filling the tank with air. This, of course, should be guarded against since a fresh supply of air means a condition for further deterioration of the fluid.

In dealings with customers it is good practice to urge a reasonable turnover of the fluid in the tank. This is a wise directive since it is known that the longer the storage time the greater the chances for increased sludging of the fluid.

Consideration should also be given to the temperature of the room where fluid is stored. Excessive fluid storage temperature, of course, tends to accelerate decomposition reactions. Direct sunlight should not be allowed to strike the tank.

These precautions are ordinary considerations for plant operations, they are repeated here for emphasis only.

Drum Storage

In the storage of fluid in drums in the field there are two primary considerations from the standpoint of temperature and light. The temperature under which fluid is stored should never exceed 50° C. (122°F.) for any period of time. In addition, the fluid should be so stored that it is protected from direct sunlight at all times. This, of course, is accomplished by suitable roofing which ordinarily is available except in extreme cases. A word of explanation is in order at this point, regarding the term "sun temperature": It has been established that if a drum of fluid is exposed to the sun in a high temperature area (120° F.), the maximum temperature of the fluid will be as much as 22° F. above the prevailing maximum air temperatures. Hence, the reason for the recommendation for storing fluid drums in the shade, especially in hot climates.

In the storage of drums care should be exercised so that the drum does not breathe air unnecessarily. This is usually accomplished by not permitting bungs to become loosened.

As to blowing air through fluid, this should not be permitted in mixing operations. The recommendation is the same as discussed previously for weigh tank storage.

Fluid is not shipped in old rusted drums. It has been demonstrated in the laboratory that rust may catalyze and accelerate decomposition reactions. However, if such a drum comes to your attention it should be marked so that the Shipping Department will be aware of its condition when it is received.

In conclusion, if a case of excessive sludging is noted in the field, it should be reported at once to those concerned. Investigation of the conditions under which the fluid was stored and laboratory analysis of the fluid will provide data for further interpretation of fluid sludging.

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