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THE ASSOCIATED OCTEL COMPANY LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT

Technical Note

TITLE: THE DECONTAMINATION OF SLUDGE FROM LEADED GASOLINE STORAGE  
TANKS - EXPERIENCE TO THE END OF 1961

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SUMMARY: An account is given in this Note of two trials that have been performed according to the Ethyl Corporation procedure for the decontamination of sludge by weathering and of one trial in which potassium permanganate was used as decontaminant. Effective decontamination was not achieved in any of these trials.

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## INTRODUCTION

It is necessary for Oil Companies to remove sludge from leaded gasoline storage tanks from time to time. The disposal of such sludge presents an increasingly difficult problem. This sludge is contaminated with T.E.L. and other organolead compounds and any technique of disposal of the sludge must include effective decontamination.

Standard practice to date has been to bury this material but space for "burial grounds" is difficult to find at some refineries. Ethyl Corporation have recommended a method of disposal in which the sludge is allowed to "weather" in the open for a few weeks and it is claimed that decontamination is thereby effected. This Note outlines the Company's experience with the "weathering" technique and with a proposed method involving decontamination of the sludge by treatment with potassium permanganate. Neither method appears to give satisfactory results.

## 2. DECONTAMINATION BY WEATHERING

### 2.1 Procedure recommended by Ethyl Corporation

During 1960, Ethyl Corporation published a procedure for the decontamination by weathering of sludge from leaded gasoline storage tanks. Essentially, this procedure involves spreading the sludge in a layer of not more than three inches in thickness on the ground. The site selected may be bare ground or it may be covered with grass or with concrete. It must be fairly smooth and sufficiently well drained to prevent water-logging and should be so located that air can circulate freely over the surface of the sludge.

It is stated that the spread sludge must be left for at least four weeks, after which it may be treated as any other non-toxic waste material. The four week period applies when the ambient temperature is above 32°F., and during this time exposure to the sun is stated to be desirable but not mandatory. The safety precautions deemed to be necessary are also given.

Ethyl Corporation provided figures showing reductions in total organic lead as below:-

Four inches thick patch (1) 43.3 p.p.m. to 0.3 p.p.m. in 31 days.  
(2) 377 p.p.m. to 19.6 p.p.m. in 42 days.

Two inch thick patch (1) 38.2 p.p.m. to 0.6 p.p.m. in 31 days.  
(2) 456 p.p.m. to 2.7 p.p.m. in 42 days.

In each of these cases, values are given separately for T.E.L. and "other organic lead", those for "other organic lead" being low and approximately constant in each of these four trials. The remarkable reductions in the total organolead content of those sludges are due to the reduction of the T.E.L. content in each case.

## 2.2 Analytical Methods provided by Ethyl Corporation

Attached to the copy of the procedure for decontamination by weathering, received from Ethyl Corporation in 1960, was a copy of their Analytical Procedure No.192. This is a method for the determination of organic lead compounds in gasoline storage tank sludge, in which tetraethyl lead and "other organolead compounds" are determined separately.

Investigations in our laboratories showed that this method did not differentiate quantitatively between T.E.L. and triethyl lead salts. Ethyl Corporation were approached in mid-1961 on this point and in August, 1961, we received their reply acknowledging that our findings were correct, but stating that their Analytical Procedure No.192 was applicable only to samples containing less than 10 p.p.m. organic lead. They also sent a copy of "Determination of tetraethyl lead and its decomposition products in gasoline storage tank sludge" which comprised four analytical procedures, "A", "B", "C" and "D". Procedure "D" was the same as Analytical Method No.192, but with a number of footnotes which had not been on the previous version. Procedures "A", "B" and "C" together enable the tetraethyl lead, triethyl lead and diethyl lead contents of a sludge to be determined. We have found these procedures to be reliable and have used them in some of the more recent work reported below. These methods have been of great value to us.

## 2.3 Weathering trial carried out in France

Early in 1961, a trial was carried out at a Mobil Oil depot at Haut-Indre, near Nantes, in which sludge from a leaded gasoline storage tank was allowed to "weather". Periodic determinations of the total organic lead content were undertaken by Octel-Kuhlmann at Paimboeuf. The analytical method used consisted of extraction of the sludge with benzene followed by destruction of the organic matter and gravimetric determination of the extracted lead. The results obtained are tabulated below:-

TABLE 1

Results of Analyses During the Trial at Haut-Indre

| Exposure time          | Total organic lead, p.p.m. |
|------------------------|----------------------------|
| As removed from tank   | 190                        |
| One month              | 200                        |
| 40 days                | 280                        |
| 50 days                | 170                        |
| 60 days                | 80                         |
| 70 days                | 70                         |
| 80 days                | 110                        |
| 90 days                | 140                        |
| 100 days               | 150                        |
| 100 days, after mixing | 340                        |
| 110 days               | 140                        |
| 110 days, after mixing | 200                        |
| 120 days               | 140                        |
| 130 days               | 200                        |

Thus, there was no significant reduction in the organic lead content of the sludge after weathering for about four months. This is certainly inconsistent with the claims made by Ethyl Corporation.

#### 2.4 Weathering trial carried out at Fawley

This trial was started during the first week in September, 1961. The sludge used was taken from a tank of 96,000 barrels capacity that had been used for several different grades of gasoline. The amount of sludge in the tank was rather less than had been expected.

The site selected for the weathering trial was a grassy patch a few feet outside the bund wall of the tank. The tank was washed down with water and the washings pumped to the weathering site. The excess liquid soon disappeared, mainly by natural drainage. The sludge was then transferred to the weathering site by wheelbarrows and spread in a layer about two inches thick. The total area covered was about 20 yards by 10 yards and of this, an area about four yards square was roped off separately and used as the test area. Half of this was raked over once per week and the other half remained unraked.

The weather during the period of the trial was typical of the English autumn and the temperature did not fall below 32°F. at any time during this period.

Duplicate samples of the "weathered" sludge were taken periodically by Esso for analysis by themselves and by this Company in order to follow the progress in decontamination, each sample comprising portions from a number of different positions on the site.

The samples taken on the 14th, 21st and 28th days that were submitted to this Company were extracted with methanol according to Ethyl Corporation analytical procedure "A" and the extract was divided into two parts. The total organic lead content was determined separately in each portion - on one by the Ethyl Corporation analytical procedure "B" and on the other by a method developed in our laboratories in which the organic lead is converted to the inorganic state and then determined by a mixed colour dithizone method at pH = 9.0.

The other samples received were divided into two parts. One part was analysed by the Ethyl Corporation procedures "A" and "B". The other portion was extracted with a solvent comprising 5 parts by volume of methanol and 2 parts by volume of carbon tetrachloride. The lead in the extract was then converted to the inorganic state and determined by the mixed colour dithizone method.

It can be seen from Table 2 that the results obtained by two methods were in satisfactory agreement on most, but not all, of the samples.

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TABLE 2

Results of Total Organic Lead Determinations During the Trial at Fowley

| Exposure time in days | TOTAL ORGANIC LEAD, EXPRESSED AS P.P.M. T.E.L. |                    |                   |                    |
|-----------------------|------------------------------------------------|--------------------|-------------------|--------------------|
|                       | Raked Portion                                  |                    | Unraked Portion   |                    |
|                       | Ass. Octel method                              | Ethyl Corp. method | Ass. Octel method | Ethyl Corp. method |
| From tank             | 149                                            | 159                | 165               | 164                |
| 1                     | 228                                            | 207                | 167               | 167                |
| 2                     | 172                                            | 156                | 135               | 132                |
| 4                     | 182                                            | 184                | 202               | 188                |
| 7                     | 156                                            | 162                | 150               | 161                |
| 14                    | 135                                            | 191                | 115               | 156                |
| 21                    | 118                                            | 170                | 109               | 138                |
| 28                    | 101                                            | 138                | 94                | 144                |
| 51                    | 85                                             | 165                | 93                | 173                |
| 66                    | 80                                             | 87                 | 83                | 74                 |
| 98                    | 86                                             | 84                 | 72                | 76                 |

Certain samples taken during this trial were analysed by Ethyl Corporation procedures "A", "B" and "C" in order to determine the relative amounts of T.E.L. and other organolead compounds present in the sludge. The results obtained, expressed as p.p.m. T.E.L. by weight, are given in Table 3.

TABLE 3

Results of Analyses for T.E.L. and "Other Organolead"

| Exposure time days | Raked Portion |                   |       | Unraked Portion |                   |       |
|--------------------|---------------|-------------------|-------|-----------------|-------------------|-------|
|                    | T.E.L.        | Other organo lead | Total | T.E.L.          | Other organo lead | Total |
|                    |               |                   |       |                 |                   |       |
| 2                  | -             | -                 | -     | 112             | 20                | 132   |
| 14                 | 159           | 32                | 191   | -               | -                 | -     |
| 21                 | 161           | 9                 | 170   | 129             | 9                 | 138   |
| 28                 | 129           | 9                 | 138   | 112             | 32                | 144   |
| 98                 | 66            | 18                | 84    | 68              | 8                 | 76    |

Thus, it was shown that the bulk of the organolead present in the sludge was present as tetraethyl lead. This is consistent with the results reported by Ethyl Corporation but the rate at which the T.E.L. disappeared from the sludge during the weathering process was very slow.

The claims made by Ethyl Corporation for the rate of decontamination were clearly not substantiated, despite the fact that the conditions under which the trial was performed were well within the range of conditions laid down by Ethyl Corporation.

### 3. DECONTAMINATION BY POTASSIUM PERMANGANATE IN AQUEOUS ACETONE

#### 3.1 Laboratory experimental work

##### 3.1.1 Treatment of sludge with various decontaminants

In October, 1958, Sales Manager, requested an investigation into the possibility of chemical decontamination of sludge from loaded gasoline storage tanks. Laboratory trials were carried out in 1959<sup>(1)</sup>, as a result of which it was concluded that the use of potassium permanganate and acetone might be the answer to this problem. In this work, the effectiveness of decontamination was assessed by measurement of lead-in-air concentration above the treated sludge and the use of potassium permanganate and acetone reduced the lead-in-air values to zero. No analyses for organic lead content, before or after treatment, were carried out.

It was recommended that this technique be investigated further and a field trial was eventually organised in 1961 (Section 3.2, below).

Meanwhile, other relevant laboratory investigations into the effect of potassium permanganate have been carried out.

##### 3.1.2 Later experimental treatment of sludge with permanganate

After the Ethyl Corporation methods of analysis were made available, they were used to examine sludge that had been treated with potassium permanganate in the laboratory. Two samples of sludge were taken and two trials were performed on each. In each trial, 25 g. of the sludge was treated with 5 ml. of acetone and a weighed amount of potassium permanganate. It was then shaken for two hours. Hydroxylamine sulphate and methanol were then added and the mixture shaken again to destroy the excess permanganate and simultaneously extract the organolead compounds. The extract was analysed according to the analytical procedures "B" and "C" and the results are given in Table 4.

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TABLE 4

Treatment of Sludge with  $\text{KMnO}_4$  in the Laboratory

| Sludge sample | Before treatment                    | Treatment              |               | After treatment                     |                                     |
|---------------|-------------------------------------|------------------------|---------------|-------------------------------------|-------------------------------------|
|               | Total organic lead as p.p.m. T.E.L. | Wt. $\text{KMnO}_4$ g. | T.E.L. p.p.m. | Other organic lead as p.p.m. T.E.L. | Total organic lead as p.p.m. T.E.L. |
| A             | 207                                 | 1.5                    | 109           | 54                                  | 163                                 |
|               | 207                                 | 2.5                    | 94            | 63                                  | 157                                 |
| B             | 80                                  | 1.5                    | 33            | 31                                  | 64                                  |
|               | 80                                  | 2.5                    | 4             | 38                                  | 42                                  |

These results show that the organic lead content of sludge is considerably reduced by the type of treatment, but that more severe conditions and longer reaction times would be needed before the sludge could be regarded as "decontaminated".

It may be noted that the values obtained for "other organic lead", i.e. diethyl lead and triethyl lead compounds, are much higher proportions of total organic lead than was the case when samples obtained during the weathering trial were analysed by the same technique.

### 3.2 Chemical decontamination trial carried out at Fawley

It was arranged that a field trial of the technique of decontamination by potassium permanganate should be undertaken at Fawley, using some of the sludge from the same storage tank as that used in the weathering trial.

A concrete mixer was charged with about 600-lb. of sludge, a sample of which was taken for determination of its organic lead content. The sludge was mixed and a lead-in-air test was made by sampling the atmosphere inside the mixer barrel.

The attempted decontamination was carried out in two stages. Firstly, a slurry of 6-lb. of potassium permanganate in 2-gallons of acetone was added, followed by mixing for 45 minutes. Secondly, a further 6-lb. of potassium permanganate in 1-gallon of acetone was added, followed by a mixing for a further 75 minutes. The contents of the mixer were then allowed to stand overnight. The sludge became a darker brown colour during the permanganate treatment, possibly due to the oxidation of ferrous iron to the ferric state, but the addition of the comparatively small volumes of acetone did not result in a separate liquid phase at any time during the trial. It was not possible, therefore, to see whether or not excess permanganate was present.

Lead-in-air tests were made inside the mixer and samples of sludge were taken for organic lead determination at the end of each stage and also after standing overnight. The results obtained are given in Table 5.

TABLE 5

Results of Analyses made during Chemical Decontamination  
Trial at Fawley

| <u>Sample</u>                  | <u>Lead-in-air</u><br><u>test inside</u><br><u>mixer</u><br><u>ug. Pb./cu. ft.</u> | <u>Total organic</u><br><u>lead content</u><br><u>of sludge as,</u><br><u>p.p.m. T.E.L.</u> |
|--------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| 1. Before treatment            | > 20                                                                               | 147                                                                                         |
| 2. After first stage           | 12.5                                                                               | 159                                                                                         |
| 3. After second stage          | 3                                                                                  | 47                                                                                          |
| 4. After standing<br>overnight | < 1                                                                                | 48                                                                                          |

These results indicate a rapid reduction of the organic lead content to about one third of the original level, but not down to a level that would indicate satisfactory decontamination, despite the very low lead-in-air concentration that was achieved.

4. DECONTAMINATION BY HEATING

It is well known that all organolead compounds are thermally unstable and can be rapidly decomposed to inorganic lead compounds by heating to fairly high temperatures. Thus, it should be possible to decontaminate sludge from loaded gasoline storage tanks by heating under controlled conditions. Such a technique would be more certain in its operation than weathering or chemical decontamination and may deserve serious consideration.

5. STANDARDS OF DECONTAMINATION

The information available from Ethyl Corporation about their "weathering" procedure includes excerpts from a Field Bulletin in which references are made to the level to which the organic lead content should be reduced.

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For example:

- (1) "If the sample taken after four weeks of weathering has a lead content of 0.002 wt. % or less, no more samples need be taken".
- and (2) "Whenever the weathered sludge analyses 0.002 wt. % organic lead or less, it may be considered safe and the sludge may then be treated as any other non-hazardous waste material".

Thus, it appears that Ethyl Corporation accept a standard of 20 p.p.m. of organic lead (equivalent to about 30 p.p.m. of T.E.L.) as indicating satisfactory decontamination. This is much less stringent than the standards that have been applied by this Company from time to time in not dissimilar circumstances. When required to assess the toxic hazard associated with gasoline tank sludge that has been buried and may have to be removed, we have tended to regard samples containing organolead compounds in amounts down to the equivalent of 3 p.p.m. T.E.L. as presenting a toxic hazard.

There is obviously a need to agree on a limiting organolead content below which this type of sludge may be considered safe to handle. Any proposed decontamination procedure can then be designed to reduce the organolead content to below the limit.

## 6. CONCLUSIONS

The claims made by Ethyl Corporation for their procedure for decontamination by weathering have not been substantiated by the results obtained from two trials in which this Company has had an interest - one in France and one in England.

The one trial that has been performed using potassium permanganate as the decontaminant in the presence of acetone was not successful although a lower total organic lead content was attained in two hours by this technique than was achieved in two months by the weathering procedure.

In order to assess the development of the permanganate method or any other procedure, it will be necessary to define "effective decontamination" in quantitative terms of the final organolead content of the sludge. The limit quoted by Ethyl Corporation may be higher than this Company would be prepared to accept.

## REFERENCE

- (1) "Decontamination of gasoline storage tank sludge", W. Towers, File Ref. No. G.12/3/15.

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