



# PATENT SPECIFICATION

NO DRAWINGS.

986.453

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**Int. Cl.:—C 23 f // C 07 c, C 10 g**

## COMPLETE SPECIFICATION

### Corrosion-Prevention Process

We, THE ASSOCIATED OCTEL COMPANY LIMITED, of 20 Berkeley Square, London, W.1, a British Company, do hereby declare the invention for which we pray that a patent

5 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In the petroleum industry, the handling, storage and use of industrial liquids such as gasoline, diesel oils, fuel oils, lead anti-knock compounds and ethylene dibromide results in corrosion and consequent rapid deterioration of the insides of storage drums, pipes, valves and the like. This corrosion causes fouling of the products, blockage of valves and jets, perforation of containers and storage vessels, and other difficulties. The rate of corrosion increases considerably when the product is saturated with water and/or the operating temperature is high, e.g. 50°—80°C. Considerable attention has been given to this problem and attempts have been made to eliminate corrosion by choosing suitable materials to construct the apparatus or by the addition of corrosion inhibitors. For example, attempts have been made to find a means of reducing the rate of corrosion of mild steel, which is widely used in the handling and storage of liquids of the petroleum industry, by ethylene dibromide; the only previously discovered additives that significantly reduce such corrosion are 4-methyl-2,6-di-*t*-butylphenol and propargyl alcohol, which cause a reduction of about 40%.

35 Investigations have now been carried out to find whether other materials would be suitable. The experimental procedures used, together with their results, are set forth in detail below, and particular attention has been given to the inhibition of corrosion by ethylene dibromide, which is commonly added to gasoline as a "scavenger" to remove lead produced during the decomposition of lead alkyls, themselves added to improve the octane rating of the gasoline. These investigations have led to

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the discovery that epichlorohydrin (1-chloro-2,3-epoxypropane) inhibits to a considerable extent the corrosion of mild steel and many alloy steels by ethylene dibromide, ethylene dichloride, lead anti-knock compounds, residual oil, diesel oil, fuel oil, and gasoline. In accordance with the present invention, epichlorohydrin is added to ethylene dibromide and to lead alkyls, diesel oils, fuel oils and gasoline in order to reduce the corrosive activity of such materials.

The lead alkyls to which the invention applies are principally lead tetraethyl, lead tetramethyl, and their physical mixtures, and lead tetraethyl and lead tetramethyl that have been chemically reacted in the presence of a catalyst to form a competent mixture.

In the application of the invention to ethylene dibromide, the preferred amount of epichlorohydrin is 0.1 to 0.5% by volume of the ethylene dibromide, although larger amounts may be added. *t*-Butyl acetate and *iso*-butyl acetate can be added to the epichlorohydrin and ethylene dibromide to stabilise the lead alkyl compound to which the ethylene dibromide will eventually be added, providing some degree of lead appreciation.

Before the investigations leading to the discovery on which the present invention is based, investigations of the corrosion of mild steel by ethylene dibromide had shown that phosphating of the metal did not appreciably affect the corrosion rate, neither did it make very much difference whether redistilled ethylene dibromide was used, although corrosion did increase with the temperature. The tests on ethylene dibromide described below were therefore carried out on unphosphated steel with warm ethylene dibromide from normal production plant which, instead of being redistilled, had been subjected to continuous steam injection to hydrolyse impurities. The number of specimens tested was as large as practicable so that a high degree of significance could be attached to the results.

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weeks, but that after eight weeks corrosion was about equal to that obtained with uninhibited ethylene dibromide and after 12 weeks the corrosion was more severe. All tests were therefore carried out over a comparatively long period of the order of 14 weeks.

The following table sets forth data for liquid-phase and vapour-phase inhibition of corrosion by ethylene dibromide by epichlorohydrin and certain other additives. Only significant results are included, although other experiments tending to confirm these results, but having an insufficient statistical significance to be included, were also carried out.

to the Commission indicated the possibility of a common and/or regional health program and the following have been identified and are being followed:

the fact that the majority of the population is still in the rural areas, and that the majority of the population is still in the rural areas, and that the majority of the population is still in the rural areas.

the use of a number of different methods which have been found to be effective in the treatment of various types of corrosion. The use of a number of different methods is necessary because the corrosion process is a complex one and the rate of corrosion is affected by many factors. The use of a number of different methods is necessary because the corrosion process is a complex one and the rate of corrosion is affected by many factors.

[illegible]

The following have now been received from the  
 various sources mentioned above, and are being  
 forwarded to the various departments for their  
 consideration. The following are the names of the  
 persons who have been appointed to the various  
 positions mentioned above, and are being  
 forwarded to the various departments for their  
 consideration. The following are the names of the  
 persons who have been appointed to the various  
 positions mentioned above, and are being  
 forwarded to the various departments for their  
 consideration.

| Test No. | Period of Test | No. of Specimens | Concentration of Inhibitor                                     | Mean wt. Loss g. | Percentage Efficiency of Inhibitor |
|----------|----------------|------------------|----------------------------------------------------------------|------------------|------------------------------------|
| 1        | 87 days        | 3 (liquid phase) | None (Control)                                                 | 0.2775           |                                    |
|          |                |                  | 0.1% MDBP + 0.01% NaNO <sub>2</sub>                            | 0.4010           | -44.5                              |
|          |                |                  | 0.5% Na <sub>2</sub> CO <sub>3</sub> + 0.01% NaNO <sub>2</sub> | 0.4417           | -74.5                              |
|          |                |                  | 0.01% NaNO <sub>2</sub>                                        | 0.5354           | -93                                |
|          |                | 3 (vapour phase) | None (Control)                                                 | 1.7480           |                                    |
|          |                |                  | 0.25% Na <sub>2</sub> CO <sub>3</sub>                          | 2.9343           | -25                                |
|          |                |                  | 0.01% MDBP + 0.1% NaNO <sub>2</sub>                            | 3.0323           | -67.8                              |
| 2        | 96 days        | 3 (liquid phase) | None (control)                                                 | 0.0231           |                                    |
|          |                |                  | 0.1% cyclohexylamine palmitate                                 | 0.3150           | -1260                              |
|          |                |                  | 0.1% diortho-tolylthiourea                                     | 0.3617           | -1470                              |
|          |                | 3 (vapour phase) | None (control)                                                 | 0.1378           |                                    |
|          |                |                  | 0.1% ECH + 0.1% IBA                                            | 0.0158           | 88.5                               |
|          |                |                  | 0.1% diortho-tolylthiourea                                     | 1.1450           | -72.5                              |
| 3        | 106 days       | 5 (liquid phase) | None (control)                                                 | 0.3329           |                                    |
|          |                |                  | 1.0% ECH + 1.0% IBA                                            | 0.1046           | 66.6                               |
|          |                |                  | 1.0% ECH + 0.5% IBA                                            | 0.1176           | 64.7                               |
|          |                |                  | 1.0% ECH + 0.1% IBA                                            | 0.1609           | 51.7                               |
|          |                |                  | 0.5% ECH + 1.0% IBA                                            | 0.1186           | 64.4                               |
|          |                |                  | 0.5% ECH + 0.1% IBA                                            | 0.1845           | 44.6                               |
|          |                |                  | 0.5% ECH + 0.5% IBA                                            | 0.1186           | 64.4                               |

TABLE (cont.)

| No       | Test No. | Period of Test | No of specimens  | Concentration of Inhibitor | Mean wt. Loss g. | Percentage Efficiency of Inhibitor | #      |
|----------|----------|----------------|------------------|----------------------------|------------------|------------------------------------|--------|
|          |          |                | 5 (vapour phase) | None (control)             | 1.6317           |                                    |        |
|          |          |                |                  | 1.0% ECH +<br>1.0% IBA     | 0.2345           | 85.6                               |        |
|          |          |                |                  | 1.0% ECH +<br>0.5% IBA     | 0.2811           | 82.7                               |        |
|          |          |                |                  | 1.0% ECH +<br>0.1% IBA     | 0.3682           | 77.5                               |        |
|          |          |                |                  | 0.5% ECH +<br>1.0% IBA     | 0.2847           | 82.5                               |        |
|          |          |                |                  | 0.5% ECH +<br>0.5% IBA     | 0.5058           | 69.0                               |        |
|          |          |                |                  | 0.5% ECH +<br>0.1% IBA     | 0.3015           | 81.5                               | 0.3015 |
|          |          |                |                  | 0.1% ECH +<br>1.0% IBA     | 0.8211           | 62.5                               |        |
|          |          |                |                  | 0.1% ECH +<br>0.5% IBA     | 0.8874           | 45.6                               |        |
|          |          |                |                  | 0.1% ECH +<br>0.1% IBA     | 1.2034           | 26.2                               |        |
|          | 4        | 124 days       | 5 (liquid phase) | None (control)             | 0.0813           |                                    |        |
|          |          |                |                  | 1.0% ECH +<br>0.5% TBA     | 0.0027           | 96.6                               |        |
| 1%       |          |                |                  | 1.0% ECH +<br>0.1% TBA     | 0.095            | 88.3                               | 0.0095 |
|          |          |                | 5 (vapour phase) | None (control)             | 0.1273           |                                    | 0.4273 |
| 1%       |          |                |                  | 1.0% ECH +<br>0.1% TBA     | 0.0100           | 97.7                               |        |
| 1%       |          |                |                  | 1.0% ECH +<br>0.5% TBA     | 0.0171           | 96.6                               | 0.07%  |
| (Liquid) | 5        | 124 days       | 5 (liquid phase) | None (control)             | 0.1543           |                                    |        |
|          |          |                |                  | 0.1% ECH                   | 0.0005           | 99.9                               |        |
|          |          |                |                  | 0.5% ECH                   | 0.0005           | 99.9                               |        |
|          |          |                |                  | 1.0% ECH                   | 0.0008           | 99.9                               |        |
|          |          |                | 5 (vapour phase) | None (control)             | 0.2293           |                                    |        |
|          |          |                |                  | 0.1% ECH                   | 0.0016           | 99.3                               |        |
|          |          |                |                  | 0.5% ECH                   | 0.0004           | 99.8                               |        |
|          |          |                |                  | 1.0% ECH                   | 0.0009           | 99.6                               |        |



—w/v for MDPB,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$ , cyclohexylamine palmitate and diorthotolylurea; v/v for ECH, IBA and TBA

MDPB=4-methyl-2,6-di-*t*-butyl-phenol

ECH=epichlorohydrin

TBA=tertiary butyl acetate

IBA=Isobutyl acetate

The percentage efficiency is calculated from the formula  
 Efficiency % =  $\frac{(\text{Weight loss of control}) - (\text{Weight loss of specimen})}{(\text{Weight loss of control})} \times 100$

It should be noted that where the inhibitor efficiency is preceded by a negative sign, an increase in corrosion is detected.

After Test 5, none of the specimens that had been immersed in epichlorohydrin-inhibited ethylene dibromide showed any signs of corrosion; most of the control specimens were covered with corrosion products. This test shows that epichlorohydrin on its own, without any added butyl acetate, has an efficiency of over 99% as a corrosion inhibitor.

Tests were also carried out to find whether epichlorohydrin with or without the addition of tertiary butyl acetate or isobutyl acetate accelerated the decomposition of lead alkyls when added with the ethylene dibromide. It was found that, while these additives tended to increase the rate of decomposition at first, the rate eventually decreased so that after some 12 weeks the total amount of inorganic lead was not significantly increased.

In the handling of diesel fuels and gasoline, carbon and many alloy steels are widely used. The corrosion increases with increase in sulphur content, as well as moisture and operating temperature. Investigations have shown that addition of epichlorohydrin, in the range 0.1 to 1.0% by volume, based on the liquid, considerably reduces the rate of corrosion of steel by specimens of those liquids. Thus, for

example, if steel test strips are partially immersed in diesel oil or fuel oil, the test strips, after 4 weeks exposure, show heavy surface corrosion in the absence of epichlorohydrin, but substantially no corrosion when 0.5% of epichlorohydrin by volume is added to the oil.

The addition of epichlorohydrin to gasoline has not been observed to result in any adverse effects in stability or engine-endurance tests; neither has any effect on octane number been observed.

The corrosion of mild steel specimens in diesel oil has been reduced in tests lasting about 300 days by the addition of 0.1—0.5 per cent by volume of epichlorohydrin.

Examination of mild steel corrosion specimens after about 300 days exposure to various types of gasoline containing lead anti-knock compounds has shown that the addition of 2 to 5 parts per million by weight of epichlorohydrin to a gasoline brings about a substantial reduction in the amount of corrosion, particularly in the vapour phase. The addition of epichlorohydrin has no adverse effect on the amount of gum formed or on the induction time. Results of these tests are set forth in

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The results

the table below:—

| Type of Gasoline      | Additives (parts per million) |      | Gum formation mg/100 ml. ‡ | Induction time minutes | Corrosion    |                |              |                |
|-----------------------|-------------------------------|------|----------------------------|------------------------|--------------|----------------|--------------|----------------|
|                       |                               |      |                            |                        | Vapour phase |                | Liquid phase |                |
|                       | MDBP                          | ECH  |                            |                        | Appearance*  | Metal loss pad | Appearance*  | Metal loss pad |
| Straight Run          | 0                             | 0    | 1.3                        | >450                   | 3            | 220            | 3            | <25            |
|                       | 0                             | 2.5  | 2.1                        | >450                   | 1            | <25            | 1            | <25            |
|                       | 0                             | 5.1  | 1.7                        | >450                   | 2            | <25            | 1            | <25            |
|                       | 0                             | 10.2 | 2.2                        | >450                   | 3            | 100            | 3            | <25            |
|                       | 0                             | 17.4 | 1.4                        | >450                   | 3            | 48             | 3            | <25            |
|                       | 17.4                          | 0    | 1.7                        | >450                   | 4            | <25            | 2            | <25            |
|                       | 17.4                          | 2.5  | 2.8                        | >450                   | 1            | <25            | 1            | <25            |
|                       | 17.4                          | 5.1  | 2.1                        | >450                   | 3            | <25            | 3            | <25            |
|                       |                               |      |                            |                        |              |                |              |                |
| Catalytically Cracked | 0                             | 0    | 4.6                        | 305                    | 2            | 115            | 2            | <25            |
|                       | 0                             | 2.5  | 8.0                        | 100                    | 1            | <25            | 1            | <25            |
|                       | 0                             | 5.1  | 5.7                        | 225                    | 3            | 125            | 2            | <25            |
|                       | 0                             | 10.2 | 5.1                        | 325                    | 3            | 100            | 2            | <25            |
|                       | 0                             | 17.4 | 4.7                        | 280                    | 2            | 120            | 4            | 99             |
|                       | 17.4                          | 0    | 5.5                        | 250                    | 3            | 76             | 3            | <25            |
|                       | 17.4                          | 2.5  | 13.0                       | 100                    | 1            | <25            | 1            | <25            |
|                       | 17.4                          | 5.1  | 5.0                        | 390                    | 4            | 79             | 3            | <25            |
|                       |                               |      |                            |                        |              |                |              |                |
| Catalytic Reformate   | 0                             | 0    | 1.4                        | >450                   | 4            | 79             | 2            | <25            |
|                       | 0                             | 2.5  | 1.5                        | >450                   | 1            | <25            | 2            | <25            |
|                       | 0                             | 5.1  | 2.4                        | >450                   | 2            | 140            | 2            | <25            |
|                       | 0                             | 10.2 | 2.7                        | >450                   | 3            | 150            | 3            | <25            |
|                       | 0                             | 17.4 | 2.5                        | >450                   | 4            | 81             | 4            | <25            |
|                       | 17.4                          | 0    | 0.8                        | >450                   | 3            | 38             | 3            | <25            |
|                       | 17.4                          | 2.5  | 1.5                        | >450                   | 2            | <25            | 2            | <25            |
|                       | 17.4                          | 5.1  | 0.9                        | >450                   | 4            | 61             | 3            | 48             |
|                       |                               |      |                            |                        |              |                |              |                |

‡NOTE 1. Solvent Washed Residue

\*NOTE 2. 1 No visible corrosion  
2 Very slight corrosion  
3 Slight corrosion  
4 Extensive light corrosion

#### WHAT WE CLAIM IS:

1. A method of decreasing the corrosion produced in storage drums, pipes, valves and the like by the following industrial liquids, viz., gasoline, diesel fuels, fuel oils, residual oils, lead anti-knock compounds, ethylene dibromide, ethylene dichloride and mixtures of such materials, which comprises adding epichlorohydrin to the said industrial liquid.
2. A method as claimed in claim 1, in which up to 1.0 vol% of epichlorohydrin is added to the liquid.
3. A method as claimed in claim 1, in which the industrial liquid is gasoline and the epichlorohydrin addition is 2 to 5 parts per million by weight.
4. A method as claimed in any preceding claim, in which *t*-butyl acetate or isobutyl acetate is added together with the epichlorohydrin.
5. A method as claimed in any one of the preceding claims, in which the industrial liquid is ethylene dibromide.

6. A method as claimed in any one of claims 1—4, in which the industrial liquid is a competent mixture of ethylene dibromide with a lead alkyl or a mixture of lead alkyls.
7. A method as claimed in claim 6, in which the lead alkyl is lead tetraethyl.
8. A method as claimed in claim 6, in which the lead alkyl is lead tetramethyl.
9. A method as claimed in claim 6, in which the mixture of lead alkyls consists of tetraethyl lead and tetramethyl lead physically mixed.
10. A method as claimed in claim 6, in which the mixture of lead alkyls consists of tetraethyl lead and tetramethyl lead that have been chemically reacted in the presence of a catalyst to form a competent mixture.
11. A method as claimed in any one of claims 1—4, in which the industrial liquid is diesel oil, a residual oil, a fuel oil or a gasoline.
12. A method as claimed in claim 11, in which the industrial liquid is gasoline containing ethylene dibromide together with a lead alkyl.



mp mp

the table below:—

| Type of Gasoline      | Additives (parts per million) |      | Gum formation mg/100 ml. ‡ | Induction time minutes | Corrosion        |                     |                  |                     |
|-----------------------|-------------------------------|------|----------------------------|------------------------|------------------|---------------------|------------------|---------------------|
|                       |                               |      |                            |                        | Vapour phase     |                     | Liquid phase     |                     |
|                       | MDBP ECH                      |      |                            |                        | Appear-<br>ance* | Metal<br>loss<br>mg | Appear-<br>ance* | Metal<br>loss<br>mg |
| Straight Run          | 0                             | 0    | 1.3                        | >450                   | 3                | 220                 | 3                | <25                 |
|                       | 0                             | 2.5  | 2.1                        | >450                   | 1                | <25                 | 1                | <25                 |
|                       | 0                             | 5.1  | 1.7                        | >450                   | 2                | <25                 | 1                | <25                 |
|                       | 0                             | 10.2 | 2.2                        | >450                   | 3                | 100                 | 3                | <25                 |
|                       | 0                             | 17.4 | 1.4                        | >450                   | 3                | 48                  | 3                | <25                 |
|                       | 17.4                          | 0    | 1.7                        | >450                   | 4                | <25                 | 2                | <25                 |
|                       | 17.4                          | 2.5  | 2.8                        | >450                   | 1                | <25                 | 1                | <25                 |
|                       | 17.4                          | 5.1  | 2.1                        | >450                   | 3                | <25                 | 3                | <25                 |
| Catalytically Cracked | 0                             | 0    | 4.6                        | 305                    | 2                | 115                 | 2                | <25                 |
|                       | 0                             | 2.5  | 8.0                        | 100                    | 1                | <25                 | 1                | <25                 |
|                       | 0                             | 5.1  | 5.7                        | 225                    | 3                | 125                 | 2                | <25                 |
|                       | 0                             | 10.2 | 5.1                        | 325                    | 3                | 100                 | 2                | <25                 |
|                       | 0                             | 17.4 | 4.7                        | 280                    | 2                | 120                 | 4                | 99                  |
|                       | 17.4                          | 0    | 5.5                        | 250                    | 3                | 76                  | 3                | <25                 |
|                       | 17.4                          | 2.5  | 13.0                       | 100                    | 1                | <25                 | 1                | <25                 |
|                       | 17.4                          | 5.1  | 5.0                        | 390                    | 4                | 79                  | 3                | <25                 |
| Catalytic Reformate   | 0                             | 0    | 1.4                        | >450                   | 4                | 79                  | 2                | <25                 |
|                       | 0                             | 2.5  | 1.5                        | >450                   | 1                | <25                 | 2                | <25                 |
|                       | 0                             | 5.1  | 2.4                        | >450                   | 2                | 140                 | 2                | <25                 |
|                       | 0                             | 10.2 | 2.7                        | >450                   | 3                | 150                 | 3                | <25                 |
|                       | 0                             | 17.4 | 2.5                        | >450                   | 4                | 81                  | 4                | <25                 |
|                       | 17.4                          | 0    | 0.8                        | >450                   | 3                | 38                  | 3                | <25                 |
|                       | 17.4                          | 2.5  | 1.5                        | >450                   | 2                | <25                 | 2                | <25                 |
|                       | 17.4                          | 5.1  | 0.9                        | >450                   | 4                | 61                  | 3                | 48                  |

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\*NOTE 2. 1 No visible corrosion  
2 Very slight corrosion  
3 Slight corrosion  
4 Extensive light corrosion

#### WHAT WE CLAIM IS:

1. A method of decreasing the corrosion produced in storage drums, pipes, valves and the like by the following industrial liquids, viz., gasoline, diesel fuels, fuel oils, residual oils, lead anti-knock compounds, ethylene dibromide, ethylene dichloride and mixtures of such materials, which comprises adding epichlorohydrin to the said industrial liquid.
2. A method as claimed in claim 1, in which up to 1.0 vol% of epichlorohydrin is added to the liquid.
3. A method as claimed in claim 1, in which the industrial liquid is gasoline and the epichlorohydrin addition is 2 to 5 parts per million by weight.
4. A method as claimed in any preceding claim, in which *t*-butyl acetate or isobutyl acetate is added together with the epichlorohydrin.
5. A method as claimed in any one of the preceding claims, in which the industrial liquid is ethylene dibromide.

6. A method as claimed in any one of claims 1—4, in which the industrial liquid is a competent mixture of ethylene dibromide, with a lead alkyl or a mixture of lead alkyls.

7. A method as claimed in claim 6, in which the lead alkyl is lead tetraethyl.

8. A method as claimed in claim 6, in which the lead alkyl is lead tetramethyl.

9. A method as claimed in claim 6, in which the mixture of lead alkyls consists of tetraethyl lead and tetramethyl lead physically mixed.

10. A method as claimed in claim 6, in which the mixture of lead alkyls consists of tetraethyl lead and tetramethyl lead that have been chemically reacted in the presence of a catalyst to form a competent mixture.

11. A method as claimed in any one of claims 1—4, in which the industrial liquid is diesel oil, a residual oil, a fuel oil or a gasoline.

12. A method as claimed in claim 11, in which the industrial liquid is gasoline containing ethylene dibromide together with a lead alkyl.



13. Lead anti-knock compounds, ethylene dibromide, ethylene dichloride, diesel oils, residual oils, fuel oils, gasolines and mixtures of such materials containing epichlorohydrin.
- 5 14. Ethylene dibromide containing epichlorohydrin.
15. A mixture of a lead alkyl with ethylene dibromide containing epichlorohydrin.
- 10 16. A product as claimed in any one of claims 13—15, in which up to 1.0 vol % of epichlorohydrin is used.
17. A product as claimed in any one of claims 13—16 and also including *t*-butyl acetate or isobutyl acetate.
18. A product as claimed in any one of claims 13—16 in which epichlorohydrin is the only additive.
- 15 19. A method as claimed in claim 1, substantially as hereinbefore described.
- 20 20. A composition containing an industrial liquid and epichlorohydrin, substantially as hereinbefore described.

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