

C.I.O.S. No. B.88

I.G. Farben.
Short Report No. 372
on

Investigations on the anti-corrosion substance H₃ 1/136 Na

An anti-corrosion substance of the I.G. Farben Höchst "H₃ 1/136 Na" containing Na was to be added to the gasoline in order to prevent the corrosion of tanks and containers especially in the presence of the so-called sump water. This substance was examined as to corrosion, behaviour in the engine, as well as its influence on the properties of the fuel.

1. Corrosion

0.05 and 0.1% solutions of the substance were tested in 0.12 leaded gasoline with 10% of water. Equilibrium in the gasoline-water mixture had been established by shaking. The corrosion metal strips, 50 by 10 mm, at 25°C were completely covered with water.

The metals used were: Iron, galvanized iron and aluminium, together as well as singly, copper, brass, electron metal and lead. The corresponding mixtures with untreated gasoline served as comparison. Mixtures with additions of H₃ 1/136 C (cyclohexamine basis) and of a Leuna product "KSE Leuna" on an ester basis were also used for comparison. The additions amounted always to the same percentage.

Table I shows the results obtained with 0.1% additions in gm/m^2 surface. One can see the good effect of all three substances as against the result for the untreated gasoline. A similar picture was obtained with solutions of 0.05% of the two Höchst substances, in table II, especially for iron. The enhanced corrosion of copper and brass with all three substances should be stressed. The fact is confirmed for H₃ 1/136 by checking of the values of table I b) marked x). It should be added that the solutions of H₃ 1/136 always showed turbidity.

Table I

Corrosion by 0.1% H₃ 1/136 Na, H₃ 1/136 C and KSE Leuna in mg/m^2 of:

a) Iron, galvanized iron and aluminium together

| Hours | H ₃ 1/136 Na 430 | H ₃ 1/136 C 340 | KSE Leuna 430 | Gasoline Untreated 430 |
|------------|--------------------------------|-------------------------------|------------------|------------------------------|
| Fe | - 0.35 | plus 0.18 | - 0.25 | - 11.4 |
| Fe (Galv.) | - 2.1 | - 0.21 | - 3.1 | - 17.4 |
| Al | - 0.8 | - 0.18 | - 0.3 | plus 13.2 |

b) Iron, galvanized iron, Aluminium, Tin, Copper, Brass, Electron Metal and Lead

| Hours | H ₃ 1/136 Na 430 | H ₃ 1/136 C 340 | KSE Leuna 430 | Gasol. Untreated 430 |
|----------|--------------------------------|-------------------------------|------------------|-------------------------|
| Fe | - 0.5 | plus 0.10 | - 0.4 | - 14 |
| Fe Galv. | - 1.1 | - 0.49 | - 1.2 | - 27 |
| Al | - 0.91 | - 0.30 | - 0.54 | - 0.4 |
| Zn | - 1.37 | - 0.34 | - 0.9 | - 20 |
| Cu | - 0.84 | - 0.63 x) | - 1.1 | - 0.2 |
| Ms | - 1.0 | - 0.42 x) | - 0.5 | - 0.2 |
| Elektron | - 0.8 | - | - 1.1 | plus 1.1 |
| Pb | - 5.5 | - | - 4.1 | - 15 |

Table II

Corrosion by 0.05% H₂ 1/136 Na, H₂ 1/136 C and untreated gasoline of:

a) Iron, galvanized iron and aluminium together

| | H ₂ 1/136 Na | H ₂ 1/136 C | Gasol. Untreated |
|----------|-------------------------|------------------------|------------------|
| Hours | 450 | 540 | 200 |
| Fe | plus 0.7 | plus 0.1 | plus 0.1 |
| Fe Galv. | - 0.9 | - 0.4 | - 2.8 |
| Al | - 0.2 | - 0.3 | plus 1.2 |

b) Iron, aluminium, copper and electron metal together

| | H ₂ 1/136 Na | H ₂ 1/136 C | Gasol. Untreated |
|----------|-------------------------|------------------------|------------------|
| Hours | 300 | 300 | 200 |
| Fe | - 0.3 | - 1.3 | - 4.0 |
| Al | - 0.5 | - 0.1 | - 0.3 |
| Cu | - 0.4 | - 0.6 | - 0.2 |
| Electron | plus 0.2 | - 0.5 | plus 0.4 |

2. Residue Formation

From the added amount of 1gm/litre one could expect a high value for the dish test. The experimental values at 220°C were:

20 - 40 mg for H₂ 1/136 Na
7.5 mg. for H₂ 1/136 C and
30 - 40 mg for KSE Leuna

The favorable result for H₂ 1/136 C is probably due to its organic basis.

As compared to 0.5 - 1.0 mg residue for pure gasoline these high residues lead one to expect residue formation in the engine too; this is shown by the following rough calculation. We have

- 1) 1 gm/litre H₂ 1/136 Na gives 0.057 gm Na sulfate corresponding to 34 mg Na i.e. 1% Na
- 2) 1cc/litre equals 1.65 gm of lead tetraethyl gives 1.85 gm of volatile lead bromide
- 3) 1 cc/litre equals 1.46 gm iron carbonyl gives 0.63 gm iron oxide

3. Influence of Additions on the Storage Quality and Artificial Ageing

The following table shows the result of some experiments designed to show the storage quality of gasoline treated with H₂ 1/136 and for the purpose of comparison, with KSE, measured by octane number and deposits.

(continued)

Table III

| | | Octane Number | | | |
|----------------------------------|--------|---------------|-----------|---------------|-------|
| | | Fresh | Stored 1) | After Test 2) | |
| <u>1st Series</u> | | | | | |
| 0.05% H ₃ 1/136 Na in | IG.103 | 89.9 | 88.0 | | |
| | 104 | 89.4 | 83.2 | | |
| 0.05% H ₃ 1/136 C in | IG.103 | 89.4 | 86.5 | | |
| | 104 | 89.2 | 88.5 | | |
| <u>2nd Series</u> | | | | | |
| Without Additive | B.4 | 89.5 | - | 87.8 | |
| 0.1% H ₃ 1/136 Na in | B.4 | 88.9 | - | 82.4 | |
| 1% H ₃ 1/136 C in | B.4 | 90.5 | - | 90.4 | |
| <u>3rd Series</u> | | | | | |
| Without Additive | in B.4 | 90.3 | 89.3 | 88.2 | 3) 6) |
| 0.1% H ₃ 1/136 Na in | B.4 | 90.3 | 89.4 | 79.5 | 4) 6) |
| 0.1% H ₃ 1/136 C in | B.4 | 90.3 | 89.4 | 89.5 | 5) 6) |
| 0.1% KSE | in B.4 | 90.3 | 89.3 | 89.1 | 6) |

- 1) Stored for 2 months
- 2) Treated with 7 atm. excess pressure of oxygen for artificial ageing
- 3) No deposition of lead salt
- 4) Much deposition of lead salt
- 5) Little deposition of lead salt
- 6) Test carried out after 6 weeks storage

A decrease of the octane number is observed with all samples after storage. These may in part be due to a change of the engine with time. This may be seen from the values for B.4 without addition in row 3. As is known, this value does not change. The gasoline with additions shows a further decrease of the octane number by 0.5-1 unit. The deposition of lead in row 3 is remarkable; it was again stronger for the Na than for the C salt. The very strong decrease of the O.N. after artificial ageing seems improbable and needs checking.

4. Behaviour in the Engine

With regard to the corrosion experiments mentioned above the substance was used for a run in a 1% solution of Flug B.4 (0.12 vol.% LTE). Continuous runs on a larger scale were carried out with small four-stroke engines on full load. Some breakdowns were experienced due to strong pitching i.e. sticking of the inlet valves after from 2 to 8 operation hours. Table IV below gives a short summary of the results; experiments 1-9 below were carried out at high, the following at normal, temperatures of the cylinder.

Table IV

x) Lower Cylinder Temperature

| Expt.No. | Fuel | Running time | Breakdown | Diagnosis |
|----------|-----------|--------------|-------------------|----------------------|
| 1 | B.4 pl.HC | 4 h 45' | Inlet valve stuck | Very heavy deposits |
| 2 | " | 4 h 55' | " " " | " " " |
| 3 | B.4 | 11 h 30' | Exhaust " " | Little Coking |
| 4 | " | 12 h 30' | " " " | " " |
| 5 | B.4 pl.HC | 3 h 30' | Inlet " " | " " |
| 6 | " | 11 h | " " " | " " |
| 7 | " | 11 h | Nil | Little deposit |
| 8 | " | 10 h 15' | " | " " |
| 9 | " | 18 h 45' | " | Medium deposit |
| 10 | " | 4 h 30' | Inlet valve stuck | Medium to heavy dep. |
| 11 | " | 2 h 45' | " " " | " " " |
| 12 | " | 5 h 30' | " " " | Medium deposit |
| 13 x) | " | 12 h | Nil | Little deposit |
| 14 | " | 2 h | Inlet valve stuck | Very heavy deposits |
| 15 | " | 11 h 45' | Nil | Medium deposits |
| 16 | B.4 | 13 h 45' | " | Little Gum |
| 17 | " | 16 h 20' | " | " " |

In the majority of cases, however, no breakdown occurs in spite of appreciable residues. An Opel engine in a car and the same engine in a stand experiment were run for 8 hours, corresponding to a distance of 500 km., with gasoline with 0.1% addition and H₃ 1/136 Na. Here again it is remarkable that the engine run with a uniform load showed considerable residues sticking to the intake valve and especially the intake manifold. The engine run with changing load in the car, on the other hand did not show any such trouble. A strong acid corrosion also occurred in the engine run on the stand, manifesting itself on the walls of the combustion chamber. These were only half as strong for a control run with the same fuel but without addition. The residues in their relative order of amounts found were Fe₂O₃, Copper and traces of Sodium. If H₃ 1/136 Na had been added. In order to obtain information on the behaviour of additions in the aero-engines, runs were carried out in the BMW 132 mono-cylinder engine. The engines were operated with a carburettor in one case; in the other case the fuel was injected into the injection stroke in order to find out the influence on the mixture distribution. No particular residues were found in the test-run with carburettor and normal load; the lubricating oil did however contain traces of Fe and Cu and about 34 mg Na₂SO₄ per litre after a run of 7 hours.

Runs carried out with injection and higher load did not show any residues either; but an increased burning off of the spark electrodes. It should be added that after one of the runs a sticking of the inlet valve occurred although sticking of the valves could not be expected for direct injection of the fuel. After a further run, the two upper piston rings stuck, both being troubles which do not ever occur otherwise.

The residues in the suction pipes and in the inlet valve under normal conditions and particularly with uniform load consist of deposits of the pure addition. The explanation for the deposits on the piston and in the region of the rings is probably this: the Na₂SO₄ is transformed into Na₂S in the atmosphere of the engine which always has reducing properties. With CO₂ this forms Na₂CO₃. The soda captures ~6.5% of the bromine contained in 6 mg-mol lead bromide which would be formed by 1-2 cc LTE. The product is thus NaBr and not the volatile PbO. This drawback could however probably be overcome by adding correspondingly larger amounts of ethylene bromide.

On the basis of the present experiments one can say that engine trouble occurs only with uniform and especially with higher loads. The use of H₃ 1/136 Na does not seem advisable under operating conditions occurring in radio units, searchlight units, board installations and travelling aero-engines.