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Veba Oil Ag

Gelsenkirchen, FRG

International Congress and Exposition
Detroit, Michigan
February 26 — March 2, 1990

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ISSN 0148-7191
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ABSTRACT

A test programme was performed involving two pairs of vehicles - each pair of the same type and model, technically matched, and equipped with emission control systems including lambda sensors and 3-way-catalysts.

The aim of the programme was to investigate the influence of gasoline containing 15 ppm Ferrocene (Dicyclopentadienyliron) on the long-term emission performance.

Vehicles were operated in a highly comparable way under typical traffic conditions encountered in the FRG. From each pair, one car was fuelled with clear, the other with Ferrocene-containing gasoline.

Effects on the exhaust emission performance were explored at intervals of about 10 000 km operation by means of the CVS method using the FTP 75 driving cycle.

The results demonstrate that Ferrocene operation resulted in lower pollutant emissions. This was confirmed when one vehicle was switched to Ferrocene operation after 40 000 km of clear operation.

Measurements of the fuel economy during test operations showed distinct improvements when vehicles were fuelled with Ferrocene-containing gasolines.

Further investigations of particulate emissions from the test cars were conducted by an independent research institute. The results show particulate emission levels to be low, with only minor changes in the particulate iron contents. No gaseous iron compounds were measured within the detection limit.

INTRODUCTION

Ferrocene - chemically defined as dicyclopentadienyliron - belongs to the class of metallocenes and consists of two parallel C_5 hydrocarbon ring systems with the iron atom located in-between.

Due to this unique chemical structure and the resulting physical-chemical properties ferrocene is used in a variety of application areas. Some of its uses, in the field of chemistry, biochemistry, physics and mineral oil products, are given in appendix, which also contains some physical, chemical and physiological properties of ferrocene.

With regard to the use of ferrocene in mineral oil products combustion improvement in heating oils is a major field of applications (1)*. By way of contrast, its well-known property of octane enhancement in unleaded gasolines is presently only used to a small extent in racing/offroad activities and in the after-market additive business (2, 4).

The octane enhancement by ferrocene, however, offers definite energetic and economic benefits in countries with significant market shares of unleaded gasoline grades (3).

Therefore, with regard to the recent development towards an increasing market penetration of unleaded gasolines in European countries, particularly in the FRG, an investigation programme on the use of ferrocene as a gasoline additive was initiated.

The test programme, still ongoing, incorporated a variety of different technical aspects.

* Numbers in parentheses designate references at end of paper.

Table 2: Technical Data of Test Vehicles

Vehicle Code	clear Ferrocene	A 1	B 1
		A 2	B 2
Manufacturer		BMW	Volkswagen
Type		318 i	Golf Gti 16 v
No. Cylinders		4	4
Displacement	(cm ³)	1754	1760
Bore	(mm)	89.0	81.0
Stroke	(mm)	71.0	86.4
Max. Power	(kW)	75	95
at Engine Speed	(min ⁻¹)	5800	5800
Max. Speed	(km h ⁻¹)	154	200
Weight	(kg)	1040	960
Injection System		Bosch	Bosch
Knock Sensor		(L-Jetronic) without	(KE-Jetronic) with
Emission Control		Lambda Sensor 3-Way-Catalyst (monolith)	Lambda Sensor 3-Way-Catalyst (monolith)
Date of Manufacture		May 1987	July 1987
Mileage before Test	(km)	< 50	< 50
Mileage after Test	(km)	85000	20000

TEST FUELS While vehicles A 1 and B 1 were operated with clear gasoline only, A 2 and B 2 were fuelled with an identical gasoline plus 15 ppm Ferrocene.

During the test programme gasolines from several refinery batches were consumed, all consisting of unleaded Premium grade ("Euro-super") with the stated octane specifications. All gasolines were additized with a high-performance type of detergent at a commonly applied concentration level.

Over the different batches of gasolines, the addition of 15 ppm Ferrocene resulted in average octane increases of RON = 0.6 and MON = 0.4 units. For the purpose of direct comparison, this Ferrocene-caused octane enhancement was not compensated, since octane adjustment would have modified the chemical composition of the ferrocene-treated gasoline batches.

Test fuels were provided from underground tanks via gasoline dispensing pumps identically to those used in service stations. Fuel quantities were measured by means of the normal calibrated dispense monitor. Additional fuel was carried in canisters for long-distance driving.

DRIVING CONDITIONS For the field test non-professional drivers were hired to drive the test cars under typical traffic conditions. Vehicles A 1/A 2 were operated in two shifts per day, resulting in a monthly average mileage of about 14 000 km.

In contrast, vehicles B 1/B 2 were operated at more moderate average mileages of about 4 000 km per month with one shift per day only.

To compensate any effects of individual driving habits, drivers switched cars daily.

The drivers were instructed to divide up their driving mileage as follows: 10 % urban, 20 % extra urban, and 70 % autobahn driving. The actual distribution was reported daily and matched the requested distribution closely for all vehicles over the entire test duration.

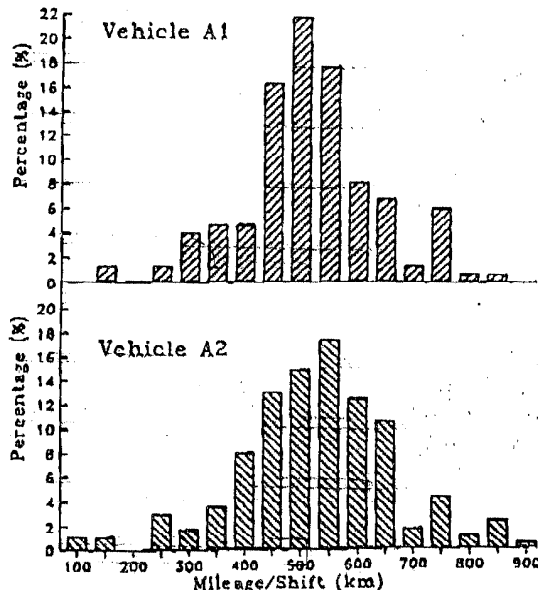


Figure 2: Mileage/Shift Distribution

From the driver records individual mileages per shift were calculated and are plotted in Fig. 2 in the form of a distribution function for vehicles A 1/A 2. The results show good agreement with peak distributions occurring at 500 - 550 km/shift, thus demonstrating that test conditions were comparable for both vehicles.

TEST RESULTS

EXHAUST EMISSION MEASUREMENTS During the field test, emissions of CO, HC and NO_x were measured at intervals of approximately 10000 km. The emission tests were conducted using the FTP 75 driving cycle on a chassis dynamometer in accordance with the regulated analytical methods. For all emission tests CEC Reference Fuel (CEC-RF-08-T-85) originating from the same fuel batch was used without Ferrocene addition.

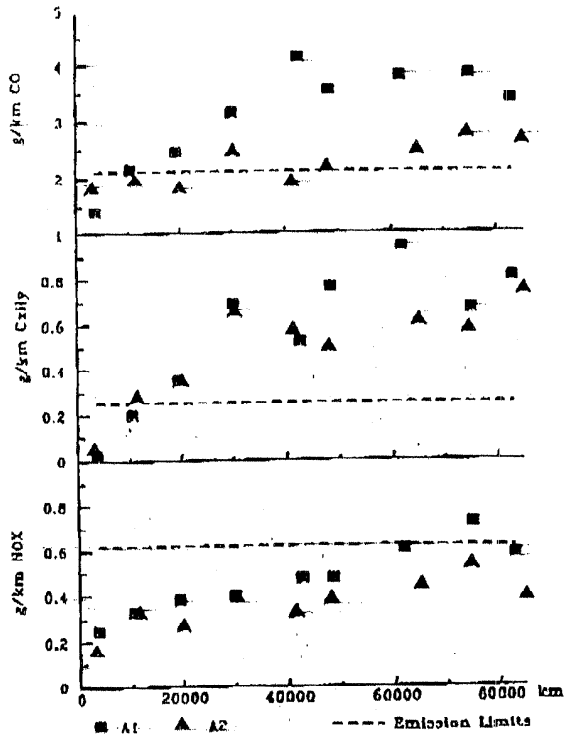


Figure 3: Exhaust Emission Measurements FTP 75 / CEC-RF-08-T-85-Fuel

Results of the CO, HC and NO_x emissions for vehicles A 1/ A 2 are shown in Fig. 3 over a test mileage of about 80 000 km corresponding to 6 months of operation. At low mileage the emissions are similar for both vehicles and emission levels are in accordance with German specified limiting values.

With increasing mileage both cars show emission increase. However, for the Ferrocene-operated car A 2 the deterioration of CO and NO_x emissions is significantly lower than for the corresponding car A1.

In the case of HC emissions both cars exceeded the specified limit after only 15 000 km of operation. Up to approximately 40 000 km no significant difference in HC emissions occurred. At higher mileages, however, Ferrocene operation again resulted in lower emission levels.

Analogue emission test results for the B 1/B 2 vehicles are shown in Fig. 4, over about 20 000 km of operation, corresponding to a test duration of 6 months.

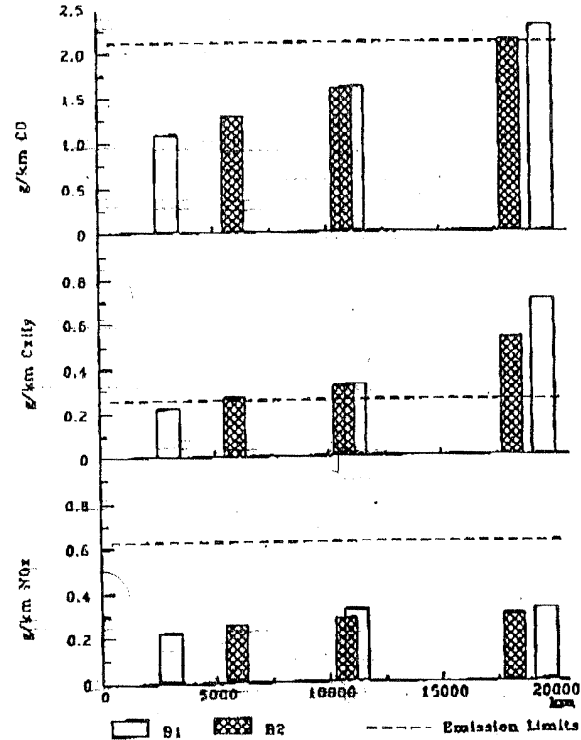


Figure 4: Exhaust Emission Measurements FTP 75 / CEC-RF-08-T-85 Test-Fuel

At the start of the test the emissions were similar for both cars and were within the specified limits. Analogue to vehicles A 1/A 2 emissions went up with increasing mileages. Up to 20 000 km the results showed no differences in the emission performance of both cars within experimental error. At this mileage, however, both cars exceeded the specified HC limit and had reached the specified CO limit. It was therefore decided to break off the comparative test at this stage.

Instead, a subsequent test was conducted with the aim of exploring changes on exhaust emission performance when an identical vehicle is switched from clear to Ferrocene operation. Vehicle B 1, therefore, was operated over a total of 40 000 km and afterwards switched to an additional 40 000 km of operation with 15 ppm Ferrocene-containing gasoline.

Emission test results obtained over both test phases are shown in Fig. 5. Again, all emission tests were performed with Ferrocene-free CEC Reference Fuel.

Fig. 5 demonstrates that the earlier observed emission deterioration continued up to 40 000 km of clear operation. Except in the case of NO_x , specified emission limits were significantly exceeded.

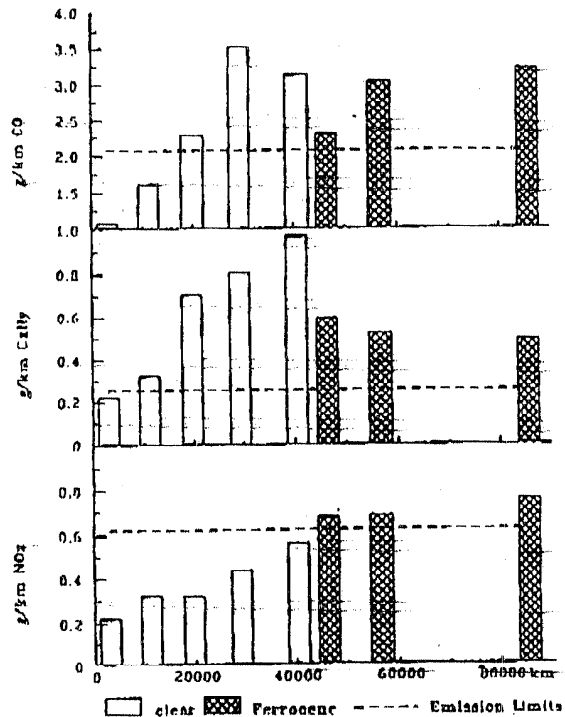


Figure 5: Exhaust Emission Measurements, Vehicle B1 FTP 75 / CEC-RF-08-T-05 Test-Fuel

After the change to Ferrocene operation a first emission measurement was taken after only 5 000 km. Results show a distinct decrease in both CO and HC emissions, while NO_x emission was unaffected. Additional measurements at higher mileages support the observed improvements due to Ferrocene.

Compared to the high HC emission deterioration during the clear phase of the test, HC emissions remained at a lower constant level during the Ferrocene operation. CO emissions, however, also increased during the Ferrocene phase. Finally, after 80 000 km of vehicle operation, the same emission level was observed as that found after only 40 000 km of clear operation.

TOV EXHAUST EMISSION RESULTS During the comparative tests an independent institution, the German Rheinisch-Westfälischer Technischer Überwachungsverein in Essen (TOV), conducted a series of emission tests on both pairs of vehicles (7).

In these tests the US Highway Cycle was applied and 30 tests were performed on vehicles A 1/A 2 at mileages of around 60 000 km. 10 tests were performed on vehicles B 1/B 2 at mileages of about 10 000 km.

Average results shown in Table 3 support the observed tendency towards improved exhaust emission performance of the Ferrocene-fuelled vehicle A 2.

Table 3: Results of Exhaust Emission Measurements by TOV

Pollutant (g/km)	Vehicle			
	A 1*	A 2*	B 1**	B 2**
CO	1.013	0.566	0.416	0.099
HC	0.062	0.044	0.025	0.019
NO_x	0.746	0.715	0.653	0.174

* Average of 30 US Highway Tests at 60 000 km

** Average of 10 US Highway Tests at 10 000 km

In contrast to the FTP emission results for vehicles B 1/ B 2, however, the TOV measurements showed significantly lower CO and NO_x emissions from the Ferrocene-fuelled vehicle B 2. A technical inspection of both vehicles showed no failure or misadjustment of relevant parts, thus providing no explanation for the emission differences.

FUEL CONSUMPTION MEASUREMENTS The evaluation of fuel economy was based on the individual refuelling operations during the field tests. This procedure provides an accurate measure of actual fuel consumption. Direct comparison of fuel economy between of A 1 and A 2 and between B 1 and B 2 is possible because comparable operation in terms of traffic and climate conditions was ensured.

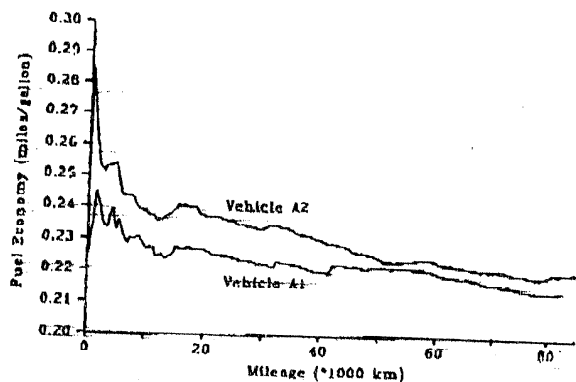


Figure 6: Cumulated Fuel Consumption - Vehicles A1/A2

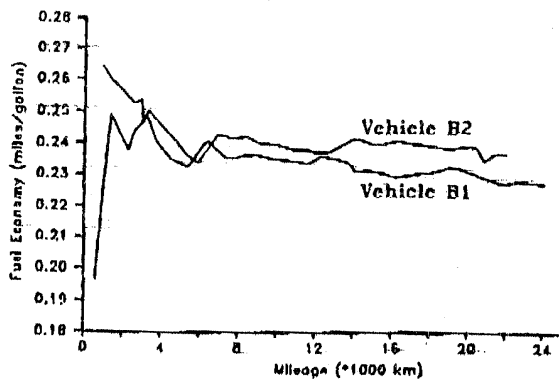


Figure 7: Cumulated Fuel Consumption Vehicles B1/B2

Fuel economy data are presented in Fig. 6 for A 1/2 and in Fig. 7 for B 1/B 2 in the form of accumulated consumption versus mileage. The results show that in both cases the ferrocene-fuelled vehicles achieved better fuel economy.

In order to verify the effect of Ferrocene on fuel economy improvement an additional test was performed using vehicle B 1 only. The vehicle was operated over 40 000 km on clear gasoline followed by another 40 000 km of operation on Ferrocene-containing gasoline.

Fuel economy data accumulated over both phases of operation are shown in Fig. 8. The results indicate an immediate improvement in fuel economy when the vehicle was switched to Ferrocene operation.

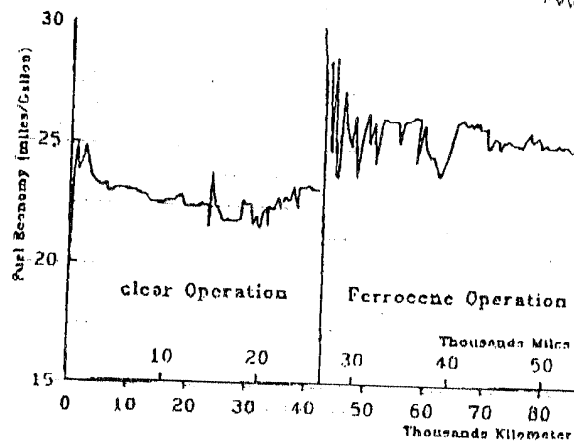


Figure 8: Cumulated Fuel Consumption Vehicle B 1

This test vehicle, however, was equipped with a knock sensor. The effect of knock sensor performance on the fuel economy was recently investigated and no significant effect was observed (8). Nevertheless, it is presently impossible to state definitively to what extent the fuel economy improvement was affected by the slightly higher octane level of the Ferrocene containing gasoline.

FURTHER EMISSION MEASUREMENTS It can be concluded that Ferrocene is combusted with the fuel to produce iron oxides. However, if combustion is incomplete either Ferrocene itself or organic iron compounds could be emitted in the exhaust gases.

Therefore, a test programme was launched to investigate the possible contribution of Ferrocene-derived combustion products on particulate and gaseous exhaust emissions.

This investigation was performed by the Fraunhofer-Gesellschaft, Institut für Umweltchemie und Ökotoxikologie (FhG), Schmallenberg, in cooperation with the Rheinisch-Westfälischer Technischer Überwachungsverein (TUV), Essen.

While TÜV conducted the driving tests and applied the appropriate sampling techniques, FhG was responsible for sample analysis. For the generation of test samples vehicles A 1/ A 2 and B 1/B 2 were used at 60 000 km and 10 000 km, respectively.

In order to obtain sufficient quantities of sample material for analysis, the vehicles had to be operated more than four hours per test on successive US Highway cycles.

During the tests exhaust gas samples were analyzed with regard to

- size distribution of particulate matter
- determination of gaseous organic iron compounds and
- quantity and iron content of particulates.

The most important results from the detailed test report provided by FHG can be summarized as follows (9):

- Impactor measurements for both vehicles clear and Ferrocene-operated - showed that the major fractions of particulates were collected in the cascade end filter with diameters < 0.1 μm .
- No organic iron compounds were determined in the exhaust gases at concentrations higher than the analytical detection limit of < 7 $\mu\text{g}/\text{Nm}^3$.
- Particulate emission levels are much lower than those from vehicles with diesel engines. Comparison of test results from clear and Ferrocene-operated cars show only insignificant increases for Ferrocene-operation with regard to particulate quantities and their iron contents.

Particulate emission data from triple measurements for A1/ A2 and a single measurement for B1/ B2 are shown in Fig. 9, while corresponding values of the particulates iron contents are compiled in Fig. 10.

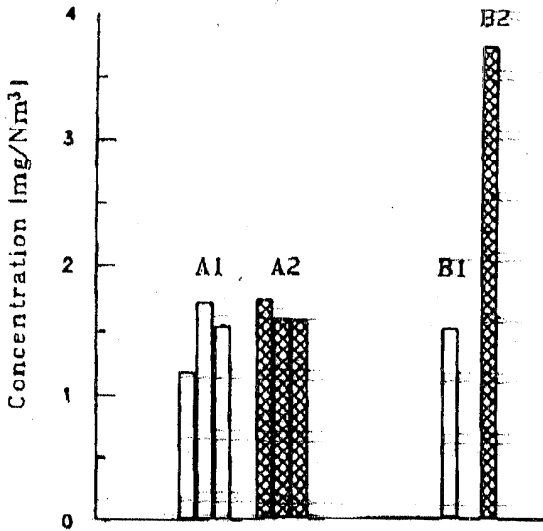


Figure 9: Exhaust Particulate Emissions. US-Highway-Test, Dilution Tunnel

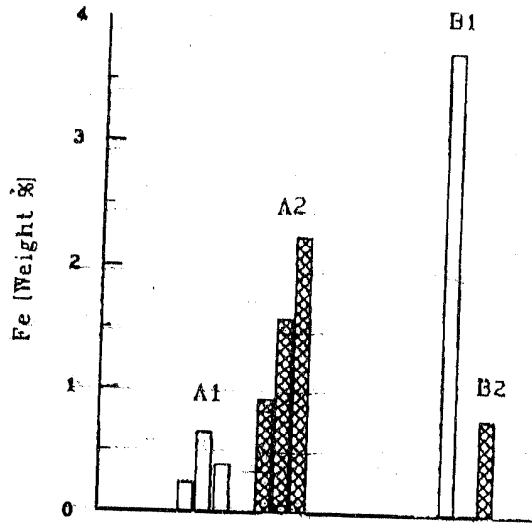


Figure 10: Iron Content of Particulates. US-Highway-Test, Dilution Tunnel

CONCLUSIONS

The present report provides test results on the use of Ferrocene as a gasoline additive.

In spite of the limited data base presently available, the test results give an indication that Ferrocene provides the following advantages:

- Octane enhancement in unleaded gasolines
- Stabilisation of emission performance in the case of emission controlled vehicles
- Improvements in fuel economy

All these effects result in environmental benefits.

While the octane increase caused by Ferrocene is readily measurable, the extent of improvements in emission performance and fuel economy may depend on the test conditions.

These were specifically selected to reflect actual German traffic conditions and can be regarded as "worst case" conditions for the US traffic situation.

REFERENCES

- (1) Somasundaram, G., and Sunavala, P.O., "Suppression of Soot in the Combustion of Residual Furnace Oil using Organometallic Additives", *Fuel*, 68 (7), 921-927 (1989)
- (2) Preuss, A.W., Schug, K.P., Höhr, D., "Method for Operating Four-Stroke Otto Engine with Ferrocene Addition to Unleaded Gasoline", *Veba Oil, Gelsenkirchen W.-Ger., Ger. DE 37 154 73* (1988).
- (3) Croudace, M.C., "Method and Fuel Composition for Control of Octane Requirement Increase, Union Oil Co. of California, U.S. US 4444565, A. 24. Apr. (1984)
- (4) Lachat, M., "Use of Dicyclopentadieny/Iron as Combustion Catalyst in Motor Fuels", *Autol A.-G., Swiss CH 599464*, 31. May (1978)
- (5) Kracklauer, J.J., "Liquid Fuel Mixtures", *Syntax USA, Ger. Offen. DE 2502307*, 31. Jul. (1975)
- (6) Hurley, R. G., Watkins, W.L.K., Griffis, R.C., "Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT", *SAE Paper No. 89 05 82*, February (1989)
- (7) Rheinisch-Westfälischer TÜV, Essen W.-Germany, "Technical Report on Exhaust Emission Tests, October (1987), unpublished client study
- (8) McNally, M.J., Benson, J.D., Callison, J.C., Graham, J.P., Wusz, T., Evans, B., "Quantifying Performance of Knock-Sensor Equipped Vehicles with Varying Octane Level Fuels - A Coordinating Research Council Program -", *SAE Paper 892037*, Sept. (1989)
- (9) Fraunhofer Gesellschaft - Institut für Umweltchemie und Ökotoxikologie, Schmaltenberg W.-Germany, "Technical Report on Particulates Size Distribution", December (1987), unpublished client study

APPENDIX

Applications

1. Effects of Ferrocene on Combustion-Processes
 - 1.1 Increase in the rate of combustion of improperly combusted hydrocarbons
 - 1.2 Combustion improvement in Gasoline- and Dieseldiengines
 - 1.3 Octane enhancement in gasoline
 - 1.4 Reduction of the smoke number of fuel oil, diesel oil and coal
 - 1.5 Improvement of the smoke point of turbine fuels
 - 1.6 Stabilisation and acceleration of combustion of solid and liquid rocket fuels and pyrotechnical products
 - 1.7 Improvement of the combustion of oil carpets floating on water
 - 1.8 Reduction of soot development from burning plastics
2. The Catalytic Effect of the Ferrocene Molecule on Reduction/Oxidation Processes is Used
 - 2.1 In the synthesis of alcohol, ammonia, lurturan, butyric acid
 - 2.2 For the combustion in fuel cells
 - 2.3 As a peroxidase in aqueous and nonaqueous solutions
 - 2.4 For the thermal decomposition of cumene hydroperoxide
 - 2.5 For the polymerisation of styrene, alkyl siloxanes, rubber, unsaturated esters, epoxy and phenol resins
 - 2.6 In the dimerisation of alkyl-phenols
 - 2.7 Flame retardancy of plastics
3. Effects of the Physical Properties

Ferrocene and its derivatives are used as a basic material, additives or as a coating in solid and liquid materials. Thereby these acquire specific properties such as:

 - 3.1 Low heat shrinkage (fibres)
 - 3.2 Thermal stability (lubricants, plastics)
 - 3.3 Photosensitivity (light-degradable foils)
 - 3.4 Light and gamma ray sensitivity (copolymers, coating)
 - 3.5 Chemical stability (plastic coatings)
 - 3.6 Dielectric stability (insulators)
 - 3.7 Semi-conductor properties
 - 3.8 Electrical conductivity
 - 3.9 Luminescence
 - 3.10 Triboelectrical charging
4. Basic Material for the Production of
 - 4.1 Biochemical agents (such as insecticides, pesticides, fungicides, growth inhibitors or agents to prevent anaemia)
 - 4.2 Organic and biochemical analysis reagents (titrants, tracers, derivation agents)

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5. Basic Material for the Production of Polymers with Functional Groups

6. Basic Material for Solar Technology - Solar Cells (photovoltaic)

7. Basic Material and Additive for Lubricants.

Physical data

	Measured value	Unit	Remarks
Formula	$\text{Fe}(\text{C}_{10}\text{H}_8)_2$	-	-
Molecular weight	186.04	-	-
Density	1.49	g/cm^3	-
Melting point	173	$^{\circ}\text{C}$	-
Boiling point	249	$^{\circ}\text{C}$	1.035 bar
Shrivel point	183	$^{\circ}\text{C}$	-
Vapour pressure	0.066	mbar	40 $^{\circ}\text{C}$
	3.4	mbar	100 $^{\circ}\text{C}$
Heat of fusion	17.8	$\text{kJ}/\text{g Mol}$	175 $^{\circ}\text{C}$
Heat of vaporization	47.2	$\text{kJ}/\text{g Mol}$	175 $^{\circ}\text{C}$
Heat of sublimation	79.2	$\text{kJ}/\text{g Mol}$	25 $^{\circ}\text{C}$
Start of decomposition	465	$^{\circ}\text{C}$	-
Magnetic susceptibility diamagnetic.			

Chemical Properties

- Its resistance to water, air, light and heat as well as the anti-corrosive effect of some of its derivatives facilitate handling and storage.
- As far as its reactivity is concerned, it is more aromatic than benzene. Therefore electrophilic reactions, such as sulphonation, FRIEDEL CRAFTS alkylation and acetylation can take place more easily on Ferrocene than on the benzene ring.

Physiological Properties

Toxic Effects on Rodent

Form of Administration	Lethal Dose LD_{50} (mg Ferrocene/kg Rodent)	
	Mouse	Rat
Oral	1.550	1.320
Intravenous	178	
Intraperitoneal	355	500

- Effect on the Organism of Mammals

Ferrocene derivatives are under discussion as agents to prevent anaemia. Orally administered Ferrocene is stored unchanged in the fatty tissue and/or is excreted in the urea as an enzymatically hydroxylated metabolite.

- Maximum Exposure Levels (MAK levels):

As no levels for exposure have yet been laid down in Germany, the figures of the American National Institute of Safety and Health (NIOSH, June 1982) have been quoted

TLV-TWA 10 mg/m^3
STEL 20 mg/m^3 DTLVS

The above-mentioned data are given to the best of our knowledge and belief but can not be regarded as binding.

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