4. Diesel Fuel Additives.

In Germany as well as in the United States considerable research work was carried forward to raise the "ignitability", the cetane rating, of diesel fuels. Additives were used, either without further treatment, in various proportions, or were added to the fuel in conjunction with some treatment such as "nitration", "ozonisation".

For convenience, the work done with various additives and the results obtained are summarized in table form.

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING Original	Resultant	Remarks
NITRATES & NITRITES					
Ethyl Nitrate	.5 to 1%	Petroleum Gas-Oil	45	53-59	Boils at 195°C; this is too low Vapour very toxic.
Ethyl Nitrate	1 to 5%	do	do	up to 72	Above 1% strongly corrosive in injection system

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING Original	CETANE RATING Resultant	Remarks
Amyl Nitrate	1 to 5%	Petroleum Gas-Oil	45	Up to 70	Quite corrosive in injection system
Iso Amyl Nitrite	1 to 5%	do	do	do	Much less corrosive than nitrate
Methyl nitrate		do	do	do	Not corrosive but boils at 122°F, too low
PEROXIDES					
Dimethyl-Peroxide	1 to 3 %	Petroleum Gas-Oil	45	-	Strong action but boiling point is 55°F
Ethylene-Peroxide	do	do	do	60	No special data
Acetone-Peroxide	do	do	do	do	Extremely explosive crystals - harm- only when dissolved.
Diethyl-Peroxide	do	do	do	do	Very effective
Diethyl-Peroxide	3%	Lignite Gasoline	25	31	Very effective
Diacetone Diperoxide	1 to 2%	Gasoil	45		Very effective
Diacetone Diperoxide	3%	Lignite Gasoline	25	34	
Diacetone Diperoxide	do	F.T.Kogasin No. 1	64	7[illegible]	

4. Diesel Fuel Additives. (Cont'd)

Used as additive	Proportion in volume	Original Diesel fuel	CETANE RATING Original	Resultant	Remarks
Monoxy-Diethyl Peroxide	1 to 2%	-	-	-	About same action as ethylene peroxide but not quite so soluble in fuels
Dioxy-Diethyl Peroxide	Less than 1%				Appears to act satisfactorily but not soluble enough
Tetraline Peroxide	3%	Lignite Gasoline	25	39	These results are questionable
Tetraline Peroxide	do	F.T.Kogasin #1	64	89	These results are questionable
Di-Benzoyl Peroxide	do	Lignite Gasoline	25	28	These results are questionable
Di-Benzoyl Peroxide	Less than 1%	Gasoil	45	up to 54	
Acetyl Benzoyl Peroxide	2%	Lignite Gasoline	25	30	
Acetyl Benzoyl Peroxide	1.2%	Gasoil	45	55	

This tabulation shows that the number of chemicals either of the nitrate or nitrite type, or of the peroxide type, that can effectively be used as additives to diesel fuels is somewhat restricted even though many may upgrade the ignitability to a considerable extent.

A further limitation is found in the solubility of some of these additives.

(a) Solubility of Peroxides in Various Fuels.

An important aspect of the addition of chemicals into diesel fuels is their solubility in the various types of oils at different temperatures. This in several cases, limits their use. In general it can be said that the solubility of peroxide additives increases as the percentage of un-saturated and aromatic hydrocarbons in the oil increases, while their solubility decreases proportionally to the percentage of paraffinic components.

Following tabulation gives the solubility of several peroxides at a temperature of 68°F (20°C):

Peroxides	Petroleum Gasoil	Kogasin I from Fischer-Tropsch	Lignite Gasoline	Leuna Gasoline (Hydrogenation of Lignite Tar)
DiAcetone di Peroxide	2.4%	4.2%	5.4%	4.2%
DiBenzoyl di Peroxide	1.2	.8	3.4	.8
Acetyl Benzoyl di Peroxide	2.2	8.2	15.4	-
Tetraline di Peroxide	1.8	4.8	16.1	3._
Diethyl di Peroxide	7 Vol.	6 Vol.	50:50	5 Vol.

(b) Effect of Peroxides on Ignitability.

Further tests were conducted at the Technische Hochschule of Munich, in a test engine where the compression ratio could be modified from 10:1 to 18:1, for the purpose of determining, with several diesel fuels and various peroxide additives, how low the compression ratio could be brought, in each case, before ignition would fail to occur.

The characteristics of the tests were as follows:

Air Temperature	86°F
Cooling Water	158°F
R.P.M.	470 ± 5
Injection Angle	17° before Top Dead Center
Torque	5 Kg/m
Injection Pressure	145 Atm.
Injector	Bosch DL 120 S 5 P 6, 5 outlets.

Below are the results, indicated in "Degrees of ignition delay, measured on the indicator diagrams", for various fuels at various compression ratios. The sign = means that no measurement was available, the sign - means "ignition fails to occur".

The reference fuel in all these tests is a petroleum gas-oil from Persian crude with a cetane rating or 45.

1st Series.. The fuel selected for the tests was a widely used type of brown coal tar oil referred to as "diesel fuel B" from the low-temperature distillation of lignite from Middle Germany (probably Saxony) with 2 percent of the additives indicated:

Compression Ratio	18	16	14	13	12	11	10
Reference Fuel	9	10	12	=	15	=	20/21
Diesel Fuel B without Additive	14	15/16	20	26/27	-	-	-
Diesel Fuel B With 2% of:							

4. Diesel Fuel Additives. (b)(Cont'd)

Compression Ratio	18	16	14	13	12	11	10
Di Methyl Peroxide	9	10/11	13	=	18	=	28
Di Ethyl Peroxide	10	11/12	13/14	=	19	25	-
Di Acetone Peroxide	11	12/13	15	=	21	27	-
Monoxydi Ethyl Peroxide	12	13	15/16	=	22/23	26/27	-
Hydrogen Peroxide	12	14	17	=	25/26	28	-
Monoperparaldehyde	13	15	19	29/30	-	-	-
Acetyl Benzoyl Peroxide	13/14	15	20	26	-	-	-

Tetralin, Dibenzoyl, Dioxy-Diethyl, etc.. show practically no difference in ignition delay.

2nd Series. Same diesel fuel "B" but with only 1 percent of peroxide additives:

Compression Ratio	18	16	14	13	12	11	10
Dimethyl Peroxide	10/11	12	14/15	=	20/21	28	-
Di Ethyl Peroxide	11/12	13	17	=	24/25	-	-
Di Acetone Di Peroxide	12	13/14	17	=	25	-	-
Ethylidene Peroxide	12/13	14/15	18	=	29	-	-
Acetylbenzoyl Peroxide	14	16	20/21	27	-	-	-

These two series of tests show the effect of even small percentages of certain peroxide additives in bringing back the ignition delay of a Diesel fuel towards the ignition delay of the reference fuel of petroleum origin. In other words it can be seen how certain additives permit the use of a synthetic diesel fuel which could not be adequately consumed without these additives at the compression ration available in certain diesel engines.

The next series of tests shows the influence of peroxide additives on the stability of diesel fuels. For every compression ratio the ignition delay is shorter when peroxides were added to the fuel before its prolonged storage.

3rd Series. A similar diesel fuel (brown coal tar) from low-temperature distillation of lignites, with 2 percent additives except as noted, and after ten months of storage.

Compression Ratio	18	16	14	12	11	10
Diesel Fuel alone	13	14	16/17	22	29/30	-
Di Aceton Di Peroxide	10	11	12/13	16	=	26
Di Ethyl Peroxide	11	12/13	14/15	18/19	23	-
Di Ethyl but only 1%	12	13	15	19	24/25	-
Acetyl Benzoyl Peroxide	12	13/14	16	21	27	-
Tetralin Peroxide	12	13/14	16	21/22	-	-
Di Benzoyl Peroxide	12	13/14	16	22	-	-

The fourth series of tests reported on the next tabulation shows that some "ignition accelerator" must be added to the diesel fuel obtained from low temperature coal tar before it can be used as diesel fuel.

4th Series. A Diesel fuel from the low-temperature distillation of coal, which does not ignite satisfactorily in the engine at compression ratio of 18:1 or below, and even at 18:1 has a 27° ignition delay, with 2 percent of various peroxide additives, or 1 percent as noted.

Compression Ratio	18	16	14	13	12
Diesel fuel without additive	27	37/38	-	-	-
Diesel fuel with:					
Diethyl Peroxide, 2%	16	18	23	30	37
Diethyl Peroxide but only 1% added	16	18	28/29	-	-
Di Acetone Peroxide, 2%	17	19/20	26	34/35	-
Di Acetone Peroxide but only 1% added	18	22	34	-	-
Mono oxy Di Ethyl Peroxide, 2%	17/18	21/22	30	-	-

4. Diesel Fuel Additives. (b)(Cont'd)

Compression Ratio	18	16	14	13	12
Acetyl Benzoyl Peroxide	18/19	22/23	31	-	-
Tetralin Peroxide	19	23	40	-	-

A final set of tests was made to see the action of the peroxide additives on a diesel fuel of petroleum origin. The same "reference fuel" is tabulated as for the first series of tests. Results show that the additives improve the ignitability of the diesel fuel beyond the quality of the reference fuel.

5th Series. Same additives in 2 percent concentration in a petroleum gas-oil (origin not known):

Compression Ratio	18	16	14	12	10	9
Reference Fuel	9	10	12	15	20/21	25
Gasoil without Additives	9/10	11	13/14	17/18	26/27	-
Gasoil with 2% of Di Ethyl Peroxide	6/7	7	9/10	11/12	16/17	22/23
Acetyl Benzoyl Peroxide	7/8	8/9	10	12/13	18	25/26
Di Aceton Di Peroxide	7/8	9	10/11	14/15	19/20	29/30
Mono OxyDiethyl Peroxide	8/9	9/10	11/12	14/15	21	29/30
Tetralin Peroxide	8/9	9/10	11/12	15	21/22	-

In addition to the better ignitability of diesel fuels containing peroxide additives, a much smoother operation and a much cleaner exhaust could be noticed.

4. Diesel Fuel Additives. (Cont'd)

(c) Effect of Other Type Additives on Ignitability.

Two additives, tried at the Technische Hochschule of Munich are worth mentioning. One is "chlorpicrin" which is "trichlor nitro methane"; added in proportion up to 4 percent it increases the cetane value materially. For instance a Kogasin II, of 92 cetane, goes up to 116 cetane by nitration and to 170 with addition of chlorpicrin after nitration. The other additive is "Lupanol", a "tetra nitro methane" which in concentrations up to 3 percent has a marked influence on ignitability.

In 1942 the Technische Hochschule in Munich conducted experiments with other organic additives. It was found that the following chemicals reduce the ignitability:

- Esters
- Cyclic hydrocarbons (like pseudocumol, cymol)
- Cyclic aldehydes (like benzoic aldehyde)
- Alcohols of low-molecular weight.

The following chemicals, on the other hand, increase the ignitability:

- Straight-chains aldehydes, in large proportion (as much as 20 percent).
- Alcohols of high molecular weight.

For alcohols in particular the following tabulation illustrates the results, and shows that, from n-Octyl alcohol up an appreciable increase in cetane rating can be noticed.

Alcohol Added	Porportion	CETANE RATING of Gasoil	After addition	Difference
Di Aceton-Alcohol	20%	45	36	-9
n - Propyl Alcohol	20%	46	37	-9
C_3	40%	46	28	-18
n - Hexyl Alcohol	20%	46	38	-8
C_6		do		
n - Octyl Alcohol	20%	do	47	+1
C_8	40%	do	51	+5

4. Diesel Fuel Additives. (c)(Cont'd)

Alcohol Added	Porportion	CETANE RATING of Gasoil	After addition	Difference
n - Nonyl Alcohol	20%	46	48	+2
C_9	40%	do	49	+3
n-Decyl Alcohol	20%	do	51	+5
C_{10}	40%	do	58	+12

(d) Effect of NITRATION on Ignitability.

Best results with high molecular alcohols were obtained when a "nitration" treatment was given the mixture, in the following manner. First a Fischer-Tropsch Kogasin I was selected and the fractions boiling below 212°F were removed. The balance had a cetane rating of 39. This was mixed with 50 percent of various alcohols, and the mixture subjected to a nitration process by bubbling gaseous concentrated nitric acid through the liquid. The results were as follows:

Percentage of NO_2 Absorbed	Increase in Cetane
.12	0
.31	0
.67	3
1.20	7
1.58	10.5
2.08 (Saturation)	18

In most of these experiments a precipitation of pitch took place, and the oil had to be filtered after the reaction.

These fuels are not corrosive unless they are from coal origin and contain phenols.

(e) Effect of OZONISATION on Ignitability.

The Technische Hochschule of Munich conducted a considerable number of tests in 1940-42 along the line of ozonisation of Diesel fuels for the purpose of raising the cetane rating. It was found that the length of contact of the diesel fuel with the ozone was important, and that the ignitability was raised regardless of the oil, for instance Ruhrbenzin (gasoline) was as susceptible to the ozonisation treatment as Kogasin. Taking a Ruhr gasoline of 47 cetane the following increases were noted:

After 3 hours ozonisation, the cetane was	58
" 6 " " " " "	74
" 9 " " " " "	106
" 12 " " " " "	114
" 20 " " " " "	130
" 24 " " " " "	140

Results of various experiments conducted in 1941-42 are summarized in the following tabulation:

PRODUCT, ADDITIVE and TREATMENT	CETANE RATING
Pure Fischer-Tropsch Kogasin I (Average)	64
Same Kogasin I with 10% CS_2	68
Same Kogasin I with 3% Di Acetone Di Peroxide	70
Same Kogasin I with 5% Nitro Benzol	72
Same Kogasin I with 3% Amyl Nitrite	74
Same Ozonised for 5 hours (1 liter)	82
Same Kogasin I with 3% Ethyl Nitrate	85
Same Kogasin I with 3% Tetralin Peroxide	89
Same Kogasin I with 3% Lupanol	96
Same treated in contact with nitric acid	98
Same ozonised 8 hours (1 liter)	100
Same ozonised 10 hours (1 liter)	100
Same ozonised 15 hours then extracted	106
Same extracted with methyl alcohol then ozonised 15 hours (1 liter)	134
Same extracted with methyl alcohol then ozonised 8 hours (1 liter)	148

PRODUCT, ADDITIVE and TREATMENT	CETANE RATING
Same extracted with methyl alcohol then nitrated	96
Kogasin I extracted, nitrated and ozonised (1 liter in 8 hours)	101
Kogasin I - simply ozonised at rate of 1 liter in 15 hours	113
Kogasin II - pure	92
Kogasin II - Nitrated	116
Kogasin II - Ozonised 5 hours	121
Pure cetane	100
Cetane treated with nitric acid	104
Cetane treated with nitric acid at 194°F	132
Cyclo-hexane	14
Cyclo-hexane treated with nitric acid at 130°F	26

The above tabulation is self-explanatory. A comparison of the results with those obtained by the mere addition of a chemical permits an evaluation of the effect of a treatment such as nitration, ozonisation, or a combination of the two processes.

(f) Object of German Research with Additives.

It is to be noted that the study of "diesel fuel additives", conducted in various German scientific activities was concentrated upon one single feature; an increase in ignitability. Extensive studies of the performance of these additives in various oils, their stability, their corrosive action, before and after combustion, were apparently not made. Neither have the investigators come in contact with any studies of real value about additives that would improve the entire process of combustion regardless of the ignitability. The reason seems to be that, up to this date, additives have not been considered as the proper method to improve a diesel fuel. The Germans efforts were rather to concentrate upon the preparation of the proper blends of oils, natural or synthetic, which would operate satisfactorily without the use of additives.