

Research Institute for Automotive Engineering and
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Report FB 1697.

The Effects of Peroxides in the Engine
and their Determination.

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Synopsis:- In order to test the reactions which take place in the engine between gasoline hydrocarbons and air or oxygen, it is necessary accurately to determine the corresponding oxidation products such as peroxides, aldehydes, ketones and acids. The peroxides primarily formed are already present in many fuels or are formed during storage. These peroxides lower the anti-knock value and also frequently cause heavy gum formation in the engine. It was absolutely necessary to determine the quantity of the active oxygen contained in the peroxides of different composition. In the experiments described in the following report, based on Koch & Pohl's (1) work, the peroxide - content was at first determined by Joule and Wilson's (2) thiocyanate method. As the results were not entirely satisfactory, some improvements were suggested, experimentally demonstrated and confirmed.

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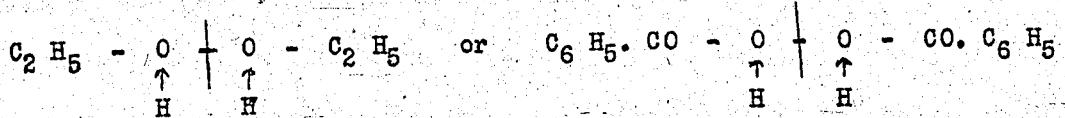
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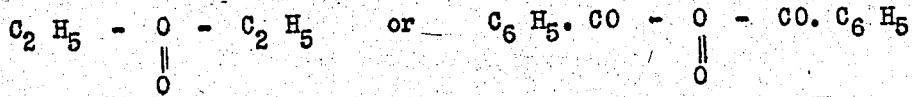
I. The chemical composition of the peroxides.

Peroxides are chemical compounds which contain active oxygen in the molecule. Hydrogen peroxide - $H_2 O_2$ - is a simple example, and may be considered as the first reduction product of the oxygen molecule. This oxygen molecule contains two oxygen atoms firmly linked together by means of two units of covalency according to the formula $O = O$. Under the influence of reducing agents they are not separated but combine with these substances with partial operation of the covalency forces to form peroxides $R \overset{O}{\sim} O$, where R is an oxidisable inorganic or organic substance, or hydroperoxides $H - O - O - H$.

The view that in peroxides the oxygen is divalent and not tetravalent as assumed in the formula $O = O \overset{H}{\underset{H}{\sim}}$ is proved by the following experimental facts:- ethyl peroxide :- $C_2 H_5 - O_2 - C_2 H_5$ and benzoyl peroxide :- $C_6 H_5 CO. O_2$. $C_6 H_5$ are smoothly decomposed into alcohol $C_2 H_5 OH$ and benzoic acid $C_6 H_5 COOH$ respectively by reduction with nascent hydrogen. This can only be reconciled with the corresponding formulae :-



respectively. It does not agree with the assumption of tetravalent oxygen according to which



respectively should result in

diethyl ether :- $C_2 H_5 - O - C_2 H_5$ and

benzoic acid anhydride :- $C_6 H_5. CO - O - CO - C_6 H_5$

respectively.

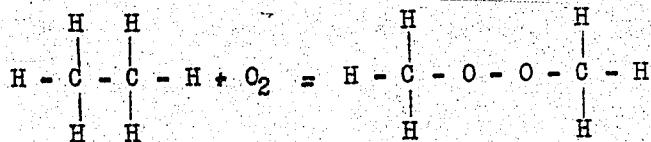
II. The effects of peroxides in the engine.

1. Influence on the knock-behaviour or the ignitability.

The peroxides already present in the fuel or formed in the engine are important

in the combustion in the engine. Some scientists as e.g. CALLENDAR (3), BENNET and MARDLESS (4) and BERL (5) assume that the peroxides are formed during the compression stroke on the surface of fine fuel droplets. The large amount of energy of the peroxides ignites the whole surrounding mixture in spontaneous combustion and thus causes knocking.

This peroxide theory is based on the assumption that an oxygen molecule can combine with a hydrocarbon molecule, as shown:-



The extent of oxidation depends upon the chemical structure of the hydrocarbons. The formation of peroxides in the cylinder during the compression stroke under certain conditions of pressure and temperature can be demonstrated. Addition of anti-knock additives to the fuel prevented the formation of peroxides.

Addition of a peroxide on the other hand causes an anti-knock fuel to knock. Thus H. SCHILDWÄCHTER (6) showed that the octane number of a gasoline depended upon the active oxygen content of the peroxide in question. At 1048 mg O₂ per litre the anti-knock value of a fuel decreased by 19 units of octane number. The tests described later show however that this fact should not lead to the general conclusion that 1 mg of active oxygen per litre causes a certain decrease of the octane number.

Thus in gasoline engine fuels, peroxides cause knocking; in Diesel engines they often increase the ignitability of Diesel fuels.

A.W. Schmidt (7) has listed the sequence of the efficiency of peroxides in Diesel fuels as follows:-

- dimethyl peroxide
- diethyl peroxide
- diacetone di-peroxide
- mono hydroxy diethyl peroxide
- acetyl benzoyl peroxide
- tetralin peroxide

2. Influence on gum formation and corrosion.

The peroxides are not only important for the mere combustion process,

they often have also the undesirable property of causing gum formation and corrosion according to their composition (6).

In studying the antioxidation and gum formation of fuels, HOCK (8) first carried out tests with tetralin and cyclohexane. These tests gave approximately 20% primary oxidation products consisting partly of peroxides. The oxidation of chain olefines was generally more difficult. The mono olefines found e.g. in synthetic gasoline are particularly stable.

The decisive factor for the stability is the position of the double bond. Conjugated double bonds are extremely sensitive to oxygen, whilst two double bonds which are far apart, act like mono-olefines. Cyclic di-olefines with conjugated double bonds are less stable than the aliphatic di-olefines.

Apart from the gum formation of fuels their corroding effect is also probably caused by derivatives of the peroxides formed initially.

3. Tests on the relation between the chemical composition of peroxides and the knock-behaviour.

(a) Chain - peroxides.

The solubility of most pure organic peroxides in gasoline is very slight, making a suitable solvent necessary in each case. Thus a 20% solution in alcohol was made in the case of dihydroxy ethyl peroxide, and added to the Leuna gasoline in quantities of 1 to 10% by volume.

The influence of the solvent - in this case alcohol - on the anti-knock value of the Leuna gasoline was first tested, and from the knock values of the alcohol - dihydroxy ethyl peroxide - Leuna gasoline blend the effect of dihydroxy ethyl peroxide on the Leuna gasoline - alcohol blend could be found. On adding 2% by weight of dihydroxy ethyl peroxide, corresponding to a peroxide content of 5241 mg O₂ per litre, it was found that the anti-knock value drops. It reduces the octane number by 8.3 units (fig.1).

Fig. 2 shows the effect of acetone peroxide on the anti-knock value of Leuna gasoline. The solvent used here was benzene. The addition of 0.69% by weight of acetone peroxide - based on the 30% per volume of benzene contained in the Leuna gasoline blend - reduced the octane number by 9.4 units. The content of active oxygen was 2982 mg O₂ per litre in this test.

Compared with dihydroxyethyl peroxide the knock - promoting effect of acetone peroxide - and the measured active oxygen content is essentially greater.

(b) Cyclic Peroxides.

Solution of cyclic peroxides in the fuel proved still more difficult. Thus at most only 18.2 gms of benzoyl peroxide could be dissolved in 100 ccs. benzene. Addition of 1.82% per weight of benzoyl peroxide to a Leuna gasoline - benzene blend containing 10% by vol. of benzene gave a decrease in anti-knock value of 5.3 units of octane number. (fig.3). A still greater reduction (6.5 units) was however obtained on adding 0.182% per weight. Thus benzoyl peroxide needs only a small addition to give its maximum drop in the octane number.

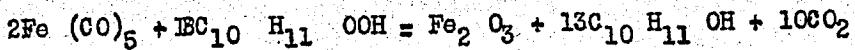
The solubility of dibenzaldiperoxide is even less. (fig.4). In this case only 0.04% per weight - containing 367 mg O₂ per litre - could be added to a Leuna gasoline blend containing 10% per volume of acetone. Here the octane number dropped only a little, i.e. approximately the same amount as on addition of 0.014% by weight of dibenzaldiperoxide. Thus dibenzaldiperoxide acts fundamentally in the same way as benzoyl peroxide, only the knock effect produced by a small quantity of additive, is greater with benzoyl peroxide.

Finally the effect of tetralinperoxide on Leuna gasoline was tested. On adding 2% by weight - containing 3900 mg O₂ per litre - the octane number dropped by 9 units (fig.5). Even with a very small addition of peroxide, the effect is also here considerable. The absolute effect increases with increase in the addition of tetralinperoxide.

The results obtained for the four organic peroxides show that the decrease of the anti-knock value is caused not only by the active oxygen content in the peroxide but that the molecular structure is also of importance.

III. Method of determination of peroxides.

There are some reactions by which the presence of peroxides or active oxygen respectively can be proved. Such reactions however, are often only used qualitatively. The oxidation of hydrogen iodide in glacial acetic acid should be mentioned as an example, the liberated iodine being titrated with sodium thiosulphate. Since iodine is known to cause side-reactions, lower values are obtained in this method, a fact confirmed by the experiments of WINDAUS and BRUNKEN (9) and also of HOCH and SUSEMIHL (10). HOCH and SCHRADER (11) examined the decomposition of ironpentacarbonyl by tetralin peroxide, which takes place according to the following reaction :-

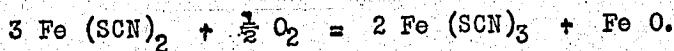


The particular difficulty is here that the iron oxide is produced as colloidal solution and can therefore not be filtered.

Y. R. NAVES (12) describes another method of determining the peroxides in ethereal oils. In this the peroxides are reduced with stannous chloride, and the hydrocarbons formed, are extracted with petroleum ether. The excess stannous chloride is back titrated with $\text{N}/100$ iodine solution in a hydrogen atmosphere. This method does not appear to be completely satisfactory according to the experiments of Hock and Schrader (11) since the extraction is complicated.

Stannous chloride was retained as a reducing agent in developing another method of peroxide estimation, and only the titration of the excess stannous chloride was adhered. This stannous chloride method, worked out by Hock and Schrader (11), has already been found satisfactory, as also has Joule & Wilson's thiocyanate method (2).

The thiocyanate method is based on the oxidation of ferrous thiocyanate according to the equation:-



The ferric thiocyanate formed is titrated with titanium trichloride.

The last two methods will now be discussed in greater detail :-

(i) The stannous chloride method.

The stannous chloride method is particularly well suited to the estimation of pure peroxides. The peroxide values of fuels it gives are found to be much lower than those obtained by the thiocyanate method.

According to Hock and Schrader's data it is important in the stannous chloride method to be able to titrate the excess stannous chloride quantitatively. Ferric chloride (13) was used in place of iodine for the oxidation.

Indigo carmine proved the most suitable indicator as it gives a good colour change from "yellow" to "blue".

The following solutions are necessary for the stannous chloride method:-

- (a) Approx $\text{N}/5$ - stannous chloride which must be kept in an atmosphere of CO_2 because of the influence of atmospheric oxygen;
- (b) $\text{N}/10$ - ferric chloride solution made from iron oxide and hydrochloric acid as titrimetric standard;
- (c) $\frac{1}{2}\%$ - indigo carmine solution;
- (d) hydrochloric acid (density $d = 1.13$)

After standardising the stannous chloride solution the peroxides are estimated as follows:-

The air had been displaced from an Erlenmeyer flask with carbon dioxide, and 10 ccs stannous chloride solution added, followed by 10 to 20 ccs of the fuel to be tested. Carbon dioxide is passed through, and the flask heated in a water bath 95°C for 5 minutes with shaking. In the case of fuels of low boiling point a reflux condenser should be fitted. The flask is then cooled down to room temperature by immersing in cold water for 2 minutes. 20 ccs hydrochloric acid and 10 drops indicator solution are added and with CO₂ still passing through the excess stannous chloride back titrated. The indicator usually changes here to "dark green".

The indicator is destroyed if the peroxides have not been completely reduced, and no colour change is obtained. Using the stannous chloride method up to 97% of the active oxygen can be determined in the case of pure peroxides.

(2) The thiocyanate method.

The following solutions are necessary for the thiocyanate method:-

(a) Reducing solution :-

5 gms. ferrous sulphate, 5 gms. ammonium thiocyanate and 5 ccs concentrated sulphuric acid are added to 500 ccs acetone and 500 ccs water and shaken vigorously for 5 minutes;

(b) N/100 - titanium trichloride solution :-

10 to 11 gms. of 15% iron free titanous chloride solution are added to N/ one litre of water and standardised against 100 - ferric chloride solution:

(c) N/100 - ferric chloride solution :-

798.4 mg A.R. ferric oxide are dissolved in 5 ccs hydrochloric acid (d - 1.13). The solution is then poured into a graduated flask containing 70 ccs of the same acid, and made up to one litre with distilled water.

The peroxides estimation is as follows:-

10 ccs of the fuel to be tested are added to 50 ccs of the reducing agent and vigorously shaken for 5 minutes. The ferric salt produced is titrated with N/100 titanium trichloride solution. The volume in ccs of N/100 titanium trichloride solution used gives the peroxide number directly after a correction, viz. mg - equivalents of active oxygen per litre of fuel. The correction is necessary because at higher concentrations of peroxides the results are always

low. It is assumed that with a peroxide number of 3.0 the value obtained agrees with the actual content. Samples richer in peroxides have either to be diluted with a peroxide free gasoline or the actual peroxide content obtained from a correction curve. But even when using this correction curve one should only use gasoline samples with a peroxide number below 10.

IV. Experience gained in using the thiocyanate method.

The thiocyanate method was first used exactly as described by Koch and Pohl (1). Apart from the great instability of the ferrous thiocyanate - acetone - water solution (reducing solution I) and the titanium trichloride solution, no particular disadvantage could be found. The reducing agent was protected from atmospheric oxygen, by storing in a brown flask in a nitrogen atmosphere. In spite of this precaution the factor of the solution changed considerably even in the course of one day.

The titanium trichloride solution behaved similarly. It was quite stable initially but after a slight turbidity had set in, it quickly became quite useless. Not much was gained by tests on the stability of titanium trichloride in presence of nitrogen, carbon dioxide and oxygen. The peroxide values were generally comparable in the three gases at the start, i.e. on the first day, but after this, it was found that the titanium trichloride could best be preserved in nitrogen. In order to achieve continuous absorption of atmospheric oxygen two gas-washing bottles filled with pyrogallol were connected before the so-called "Derona" burette (fig.6) and the titanium trichloride solution covered with a layer of nitrogen.

(1) Ferrous thiocyanate as a reducing agent in acetone - water solution (reducing solution I)

The peroxide determination by the thiocyanate method was at first carried out with arbitrarily selected fuels, and it was found, in agreement with the results obtained by Koch and Pohl (1), that the reproducibility of the results was very good. (Table 1).

Table 1 shows that oxidation of ferrous thiocyanate by peroxides took place both on shaking and on refluxing. As will be seen later, changes had to be made in order to determine the pure organic peroxides quantitatively. The results obtained from the two methods of treatment do not differ much for the fuels given in the Table 1.

The thiocyanate method was again checked with pure peroxides. It was

found that the cyclic peroxides in particular gave great difficulties. According to Koch and Pohl (1) it is possible to overcome these difficulties to a large extent by strong dilution or use of correction curves. Extensive tests on tetralin peroxide, a compound also examined by Koch and Pohl, showed that approximately 90% of the active oxygen can be determined at a suitable dilution. With benzoyl peroxide, however, only about 40% could be determined. (Table 2).

With the aid of correction curves plotted for tetralin peroxide (fig.7) with various organic diluents it is possible to show that the peroxide values obtained vary for each solution or diluent. The curves show furthermore that experimentally determined peroxide numbers below 3 do not generally agree with those calculated in each case. This means that for each test a special correction curve would have to be plotted. Only for peroxide numbers in the neighbourhood of 1 did experimental and calculated values nearly agree for most of the diluents tested. The correction curves plotted for RCH - oil (fig.8) are considerably flatter than those for tetralin peroxide and show no comparable values for any diluent.

(2) Ferrous thiocyanate as a reducing agent in alcohol - water solution (reducing solution II)

Since the thiocyanate method was not entirely satisfactory for the determination of pure peroxides when the acetone - water solution was used, attempts were made to obtain a satisfactory result with another reducing solution. The ferrous thiocyanate was no longer dissolved in acetone but in alcohol. It was immediately apparent that the ferrous thiocyanate - alcohol - water solution (reducing solution II) was much more stable than the thiocyanate - acetone - water solution. This means that the standardisation of this solution changed only a little in the course of time. Table 3 shows that quite good peroxide values were obtained using reducing solution II as soon as alcohol was not only used as solvent for the ferrous thiocyanate but also as a diluent. Compared with the reducing solution I the values are on the whole a little higher. This has a particularly favourable effect with pure peroxides. Even fuels of extremely high peroxide content - as e.g. samples J and K give a sufficient degree of repeatability in peroxide values.

The peroxide values increase further on dilution and reach their maximum at a peroxide number of about one, agreeing approximately with the calculated value. Table 3 shows also that titration in a nitrogen, hydrogen, or carbon

dioxide atmosphere alters the result very little. This can also be seen from fig. 9 and fig. 10 which show the correction curves for tetralinperoxide and RCH- oil using reducing solution II. Even the reducing solution II did not give any useful peroxide values for benzoyl peroxide, since the active oxygen is combined in a very stable form in the molecule. Therefore the benzoyl peroxide solution in alcohol had to be boiled with the reducing agent under reflux.

This led to results which were considerably better. This will be shown later in connection with the tests on other pure peroxides. Normal fuels can also be tested in this manner as shown in Table 1. It is noteworthy that in the case of benzoyl peroxide the undiluted solution yields the maximum or the same peroxide values as diluted solutions.

After extensive tests the following directions for the peroxide determination were worked out :-

10 ccs of the fuel to be tested are boiled under reflux on a water bath for one minute, together with 50 ccs of a alcohol - water solution (1 : 1) containing 5 gms ferrous sulphate, 5 gms ammonium thiocyanate and 5 ccs concentrated sulphuric acid per 1 litre. The volume in ccs of $\text{N}/100$ titanium trichloride solution used indicates the peroxide number, i.e., mgm - equivalents of active oxygen in 1. litre gasoline.

It is also suggested to abolish the correction curves, since fig. 9 and fig. 10 show that the peroxide number obtained using the reducing solution II does not agree with the actual value, even when the former is below 3. Therefore the limits of error can be kept small only by selecting a dilution for each peroxide determination which gives a peroxide number of 1 to 1.5 for the fuel to be tested.

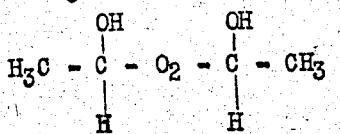
A series of organic peroxides which were not readily available otherwise were prepared in this Institute according to the directions of RIECHE (14), and tested for their content of active oxygen (peroxide number) by the above method.

They were

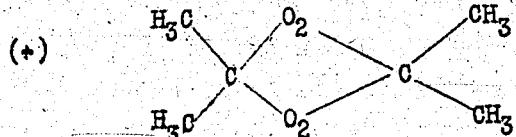
(a) Tetralin peroxide $\text{C}_{10}\text{H}_{11}\text{OOH}$

(c) Benzoyl peroxide $\text{C}_6\text{H}_5\text{CO} - \text{O}_2 - \text{COC}_6\text{H}_5$

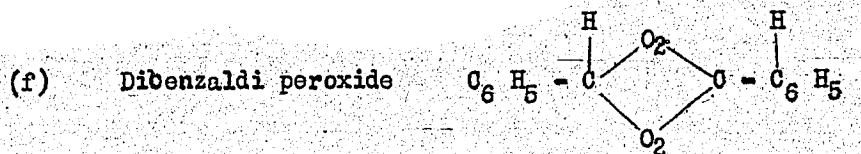
(d) Dihydroxy peroxide



(e) Acetone peroxide



(+) See line 7 next page.



These peroxides were treated with various solvents giving the active oxygen values shown in Table 4. The maximum peroxide values were obtained using alcohol as a diluent. Although the peroxides were often not absolutely chemically pure, the results obtained were satisfactory, but only if alcohol was used as a diluent. The majority of the other diluents gave wrong peroxide values.

(+) It should be noted here that acetone peroxide in the form of crystals is highly explosive. The decomposition of one crystal may cause a most violent explosion.

Generally speaking it may be said that the peroxide determination by the thiocyanate method depends principally upon the right use being made of the diluent.

V. Comparison of the reducing solutions I & II and the solubility of the peroxides.

As was mentioned before the only difference between the solutions I & II is that in one case the ferrous thiocyanate is dissolved in acetone - water, and in the other case it is dissolved in alcohol - water. This shows the extent to which the solubility of the peroxides is of importance for their quantitative determination. Whilst the pure organic peroxides are practically insoluble in the hydrocarbons contained in the fuel, they usually dissolve easily in ethyl alcohol. This solubility is increased by the fact that the oxidation of ferrous thiocyanate to ferric thiocyanate by the peroxides under test is done at 95°C on a waterbath. The lower the solubility of the peroxides in the diluent the smaller is their reactivity.

The fact that the results depend upon the solubility of the peroxides makes it absolutely necessary to give up using correction curves, and the peroxides must be determined at as high dilutions as possible.

VI. Summary.

Peroxides often reduce the anti-knock value of gasoline - engine fuels and cause gum formation. They can increase the ignitability of Diesel fuels.

Some practical tests showed that the Aliphatic peroxides especially reduce the anti-knock value of the gasoline engine fuels considerably. The reduction

of the anti-knock value, however, is not only determined by the content of active oxygen in the peroxide but mainly by the molecular structure.

In order to examine peroxide formation, it is necessary to be able to test the peroxides quantitatively.

After a critical review of the methods proposed for peroxide estimation Joule and Wilson's thiocyanate method (2) was tested. In this method ferrous thiocyanate is used as a reducing agent and N/100 titanium trichloride solution for the titration.

From the experience gained with this method, the following suggestions are made for its improvement:-

- (1) Instead of the ferrous thiocyanate solution in acetone, an alcoholic solution should be used. This solution is more stable and is a better solvent for pure peroxides.
- (2) Instead of shaking the fuel under test for 5 minutes with the ferrous thiocyanate solution to give oxydation to ferric thiocyanate, it should be boiled under reflux for 1 minute at 95°C, as this also allows estimation of cyclic peroxides.

VII References

- (1) H. Koch und H. Pohl, Zur Bestimmung des Peroxydgehalts von Kraftstoffen, Brennstoffchemie vol.19 (1938) p.201
- (2) Joule und Wilson, Ind. Eng. Chem. vol.35 (1931) p.1254.
- (3) H.L. Callendar, Engineering vol.121 (1926) p.457 und vol.123 (1927) p.147.
- (4) A.J. Bennet und W.J. Mardless, J.C.S. (1927) p.3155
- (5) E. Berl, Z.physik. Chem. vol.148 (1930) p.261
- (6) H. Schildwächter, Brennstoffchemie vol.19 (1937) p.117
- (7) A.W. Schmidt, 14. techn. Tagung des mitteldeutschen Braunkohlenbergbaus am 17./18.4.1936 Wilhelm Knapp, Halle/Saale 1936, p.535
- (8) H. Hock, Techn.Mittl. Gemeinschaftsorgan der Technik vol. 39 (1939) p.278
- (9) Windaus und Brunken, Liebigs Ann. Chem. vol.460 (1928) p.225.
- (10) Hock und Susemihl, Ber.Dtsch Chem. Ges. vol. 66 (1933) p.61
- (11) H. Hock und O. Schrader, Brennstoffchemie vol.18 (1937) p.6.
- (12) Y.R. Naves, Parfumes de France vol.10 (1932) p.225.

- (13) W. Schluttig, Z.anal. Chem. vol.70 (1927) p.55.
(14) A. Riecho, Alkylperoxyde und Ozonide, Th. Steinkopf, Dresden und Leipzig 1931.
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Illustrations

- Fig.1. Effect of dihydroxyethylperoxide on the anti-knock rating of Leuna gasoline.
- Fig.2. Effect of acetoneperoxide on the anti-knock rating of Leuna gasoline.
- Fig.3. " " Benzoylperoxide " " " " " "
- Fig.4. " " Dibenzaldiperoxide " " " " " "
- Fig.5. " " Tetralinperoxide " " " " " "
- Fig.6. Derona burette for peroxide estimation with titanium trichloride solution.
- Fig.7. Correction curves for tetralin peroxide with various organic diluents
(ferrous thiocyanate in acetone - water solution).
- Fig.8. Correction curves for RCH - oil with various organic diluents (ferrous
thiocyanate in acetone - water solution).
- Fig.9. Correction curves for tetralin peroxide with various organic diluents
(ferrous thiocyanate in alcohol - water solution).
- Fig.10. Correction curves for RCH - oil with various organic diluents (ferrous
thiocyanate in alcohol - water solution).

TABLE 1

Estimation of Peroxide in Various Fuels

Sample	Quantity Used ccs.	Dilution (n-gasoline)	Consumption of N/100 Ti Cl ₃ in ccs. Shaking	N/100 Boiling	Peroxide Number Shaking	Peroxide Number Boiling
1	10	1:10	2.4	2.5	2.4	2.5
1	10	1:1	1.25	1.35	2.5	2.7
1	10	1:1	1.2	1.35	2.4	2.7
2	10	1:2	2.6	2.7	5.2	5.4
2	10	1:2	2.65	2.65	5.3	5.3
3	10	1:0	0	0	0	0
4	10	1:10	8.1	8.25	89.1	90.75
4	5	1:10	4.25	4.35	93.5	95.7
4	10	1:10	8.0	8.25	88.0	90.75

TABLE 2

Estimation of Active Oxygen in Tetralin Peroxide
and Benzoyl Peroxide

ccs.	1 gm tetralin- peroxide in 100 ccs alcohol.	Peroxide Number	mg tetralin- peroxide found	Theoretical tetralin- peroxide content in mg.
	Dilution with n-gasoline	Shaking Boiling	Shaking Boiling	
10	1:5	36.5	34.54	28.32
10	1:10	59.92	52.26	42.85
10	1:100	112.1	110.5	90.61

ccs.	0.5 gm Benzoyl Peroxide in a 100 ccs alcohol	Peroxide Number	mg Benzoyl- peroxide found	Theoretical Benzoyl- peroxide content in mg.
	Dilution with n-gasoline	Shaking Boiling	Shaking Boiling	
10	1:2	13.9	17.9	16.82
10	1:5	9.8	16.9	11.86
10	1:10	9.7	16.2	11.74
				19.60
				50

Numerical Table 3

Sample	Quantity used ccs	Dilution	Solvent used for Ferrous thiocyanate	Peroxide Number		
				N_2	H_2	CO_2
A	10	1:0	Alcohol: H_2O (1:1)	0	0	0
B	10	1:0	"	0	0	0
C	10	1:0	"	0.28	0.28	-
D	10	1:0	"	0.94	0.96	-
E	10	1:0	"	1.24	1.24	-
F	10	1:0	"	0.22	0.28	-
G	10	1:0	"	0.2	0.23	-
H	10	1:0	"	3.45	3.6	3.75
H	10	1:2	"	7.69	7.9	7.8
H	10	1:2	"	7.5	7.45	7.85
H	10	1:2	"	7.6	7.4	7.7
H	10	1:2	Acetone: H_2O (1:1)	7.38	7.75	7.65
H	10	1:2	"	7.56	7.65	7.8
J	10	1:0	Alcohol: H_2O (1:1)	66.76	72.25	70.34
J	10	1:100	"	764.7	-	-
J	1	1:10	"	745.65	-	-
J	1	1:50	"	1188.87	-	-
J	1	1:50	Acetone: H_2O (1:1)	1170.84	-	-
K	10	1:10	Alcohol: H_2O (1:1)	40.1	-	-
K	1	1:30	"	425.76	-	-
K	1	1:30	Acetone: H_2O (1:1)	435.02	-	-

Table 4
Estimation of Active Oxygen in Organic Peroxides

Amount used 10 ccs Dilution 1:10

Solvents:-

Weighing in per 100 mg in 100 ccs	<u>Solvents:-</u>											
	Alcohol Peroxide number	Peroxide mg peroxide	Benzene Peroxide number	Benzene Peroxide mg peroxide	n-Gasoline Peroxide Number	n-Gasoline Peroxide mg peroxide	n-Heptane Peroxide Number	n-Heptane Peroxide mg peroxide	Iso-octane Peroxide Number	Iso-octane Peroxide mg peroxide	Acetone Peroxide Number	Acetone Peroxide mg peroxide
Tetralin Peroxide	12.67	10.4	9.14	7.5	7.84	6.43	8.2	6.72	7.46	6.12	10.9	8.94
	13.74	11.3	9.39	7.7	7.56	6.2	8.08	6.62	8.08	6.62	12.1	9.92
	12.25	10.04	10.5	8.61	6.92	5.7	8.64	7.1	9.22	7.6	10.8	8.9
Benzoyl Peroxide	7.08	8.6	4.3	5.20	3.5	4.23	5.8	7.02	5.9	7.14	-	-
	6.89	8.34	4.1	4.96	3.2	3.9	5.4	6.53	5.6	6.8	-	-
	7.15	8.65	3.9	4.72	3.9	4.72	5.9	7.14	5.5	6.65	-	-
Dihydroxyethyl Peroxide	11.65	7.12	8.0	4.9	6.9	4.21	7.2	4.4	6.5	3.97	11.3	6.9
	11.93	7.3	6.5	3.97	5.9	3.6	6.4	3.91	7.0	4.28	11.3	6.9
Dihydroxybutyl Peroxide	12.1	10.8	7.3	6.50	6.2	5.52	6.5	5.8	7.35	6.55	9.8	8.73
	11.2	9.98	8.2	7.31	5.4	4.81	5.3	4.72	6.9	6.15	10.2	9.1
	10.9	9.71	6.9	6.15	5.0	4.45	6.0	5.35	6.4	5.70	9.9	8.82
Acetone Peroxide	31.1	11.51	8.1	3.0	11.4	4.22	17.0	6.30	15.5	5.73	25.7	9.51
	31.7	11.73	7.0	2.6	10.2	3.77	16.15	5.97	17.0	6.3	25.7	9.51
	30.9	11.43	8.4	3.11	12.5	4.63	14.8	5.48	14.65	5.42	24.2	8.95
Dibenzal diperoxide	6.2	7.56	2.58	3.15	2.58	3.15	2.93	3.57	2.58	3.15	4.0	4.88
	5.8	7.08	1.93	2.35	2.36	2.88	3.64	4.44	3.04	3.71	3.7	4.51
	5.95	7.26	2.24	2.73	1.98	2.41	3.72	4.54	2.8	3.42	3.85	4.7