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DEUTSCHE LUFTFAHRTFORSCHUNG

REPORT No. 1742

The Effect of Aldehydes in the Engine and their Quantitative
Determination.

From examination of the effect of storage on the composition of different fuels it is known that besides peroxides aldehydes are also present. These aldehydes can be regarded as secondary oxidation products of hydrocarbons; they are present in a definite equilibrium proportion to the peroxides; they tend to give polymerisation products and influence the combustion in the engine and the residue formation.

The quantitative determination of these aldehydes is subject to certain difficulties, as the reaction depends to a large extent on the total composition of the molecules. From the different processes which have been carried out the results obtained with hydroxylamine hydrochloride were found to be the best.

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CLASSIFICATION

I. Chemical composition of the aldehydes.

II. The effect of aldehydes in the engine.

1. The effect of aldehydes on the combustion process.

2. Gum formation by aldehydes.

III. Procedure for the quantitative determination of the aldehydes.

1. Known procedures for the determination of aldehydes

2. The application of individual processes for aldehyde determination in fuels.

3. Aldehyde determination with hydroxylamine hydrochloride

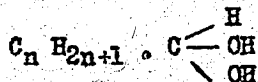
IV. Determination of aldehydes in the presence of peroxides and acids

V. Summary

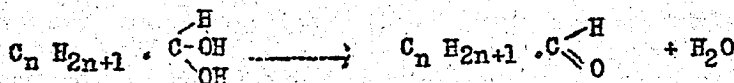
VI. Literature

I. Chemical composition of aldehydes.

If one imagines the last C atom of a hydrocarbon chain to have two OH groups in place of 2 H - atoms, then one obtains the so-called aldehyde hydrates, viz.



These aldehyde hydrates are not stable in the free state and they decompose into aldehydes by losing H_2O , as seen by the following equation:

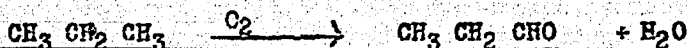


That is, aldehydes are derivatives of hydrocarbons with a $\begin{array}{l} \nearrow H \\ \searrow O \end{array}$ group at the end of the chain.

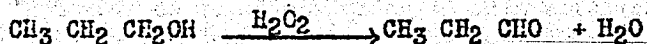
Their name is derived from "alcohol dehydrogenates" and means that the aldehydes are obtained by removing H_2 from the alcohols. The individual members are named after the corresponding carboxylic acids, e.g. acetaldehyde $CH_3 \cdot CHO$, Butylaldehyde $C_3H_7 \cdot CHO$, capron aldehyde $C_5H_{11} \cdot CHO$ etc.

The aldehydes can be formed in the following ways:

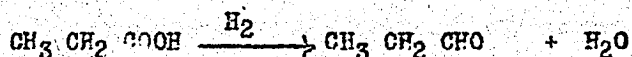
1) By oxidation of aliphatic hydrocarbons:



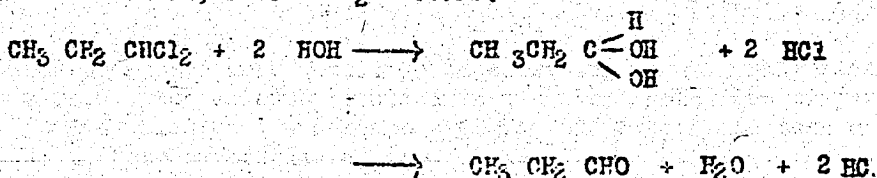
2) By oxidation of primary alcohols:



3) By reduction of compounds in a higher state of oxidation.



4) By hydrolysing halogenated hydrocarbons with two halogen atoms at the end of the chain; loss of H_2O occurs:



other preparations of aldehydes are of no interest here.

II. The Effect of Aldehydes in the Engine.

In contrast to the behaviour of the peroxides in the engine of which some lower the anti-knock value of the gasoline engine fuel considerably, the aldehydes or more accurately the $-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{OH} \\ \diagdown \\ \text{OH} \end{array}$ group is practically without effect.

In spite of this it can disturb the normal operation in the engine indirectly. High molecular compounds are easily formed from it which are strongly inclined to resin formation and thus cause ring sticking.

1) The Effect of Aldehydes on the Combustion Process: It is very difficult to determine the effect of the aldehyde group in the engine as the entire molecular structure influences the combustion process. This is illustrated by the experiments carried out with butyl aldehyde and benzaldehyde.

Fig. 1 shows how butyl aldehyde changes the anti-knock value of pure and lead containing Leuna-gasoline. Though pure Leuna-gasoline does not react noticeably to butyl aldehyde, the anti-knock value of Leuna-gasoline containing lead is influenced to a small extent already by small quantities of butyl-aldehyde ($\text{C}_4\text{H}_9\text{CHO}$). The length of the aliphatic hydrocarbon chain is the main influencing factor in lowering the anti-knock value.

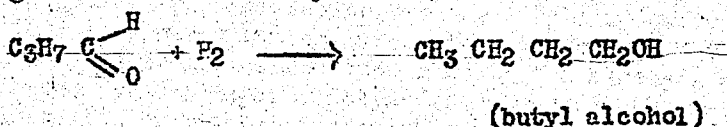
An aromatic aldehyde, viz. benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) was now added to the Leuna-gasoline. From fig. 2 it can be seen that for pure Leuna-gasoline a small increase in the anti-knock value occurred when the benzaldehyde was added. This increase in the anti-knock value is however not reducible to the $-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{OH} \\ \diagdown \\ \text{OH} \end{array}$ group but to the hydrocarbon-ring (benzene ring). The influence of benzaldehyde upon Leuna gasoline containing lead is correspondingly less. In other words the influence of the aldehyde group upon the anti-knock value is very small.

2) Gum Formation by Aldehydes: Compared to numerous materials aldehydes are strongly reactive.

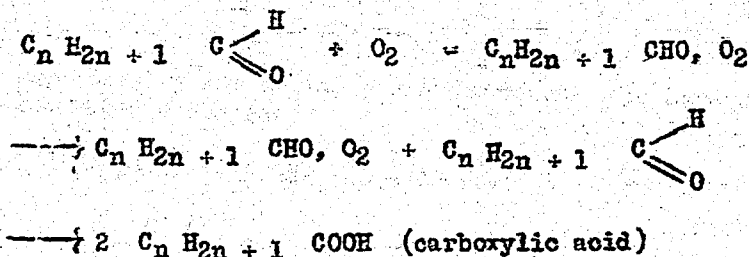
Many saturated aliphatic and aromatic aldehydes, as e.g. n - dodecylaldehyde ($C_{12}H_{25}CHO$) and benzaldehyde (C_6H_5CHO) when exposed to ultraviolet rays split off $>C=O$ and became hydrocarbons. The reactive position in the aldehyde molecule is the carbonyl group $>C=O$. This $>C=O$ group is very suitable for the formation of addition products. In the following some examples are illustrated.

a) H_2O adds on to aldehydes in aqueous solutions practically in all cases which can be recognised by the fact that solutions of aldehydes show no or very little absorption in the ultraviolet. In the presence of a carbonyl group absorption should take place.

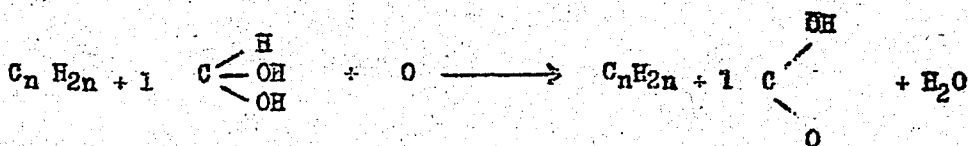
b) Hydrogen reacts with aldehydes to give primary alcohols:



c) Aldehydes are very sensitive to oxidising agents. Many aldehydes oxidise already when allowed to stand in the air. Peroxides or peracids are formed which easily decompose giving off oxygen and then combine with it to form carboxylic acids.

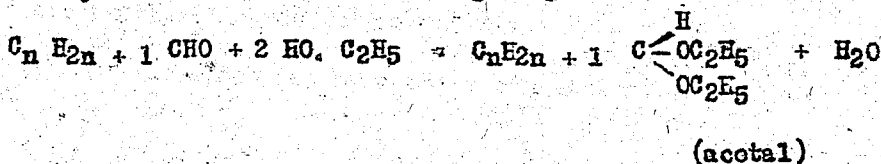


In aqueous solutions the reaction takes place in such a way that the oxygen combines directly with the two hydrogen atoms of the aldehyde hydrate:



Thus it is possible to use other substances which combine with hydrogen in place of oxygen, e.g. chinon ($C_6H_4O_2$)

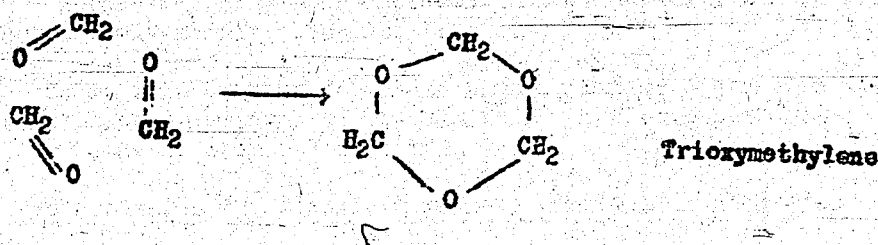
d) Aldehydes combine with alcohols giving acetals:



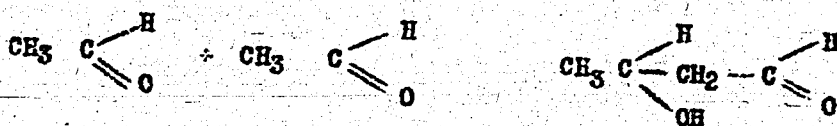
These acetals are often found as side products in the oxidation of alcohols.

- e) The reactivity of the aldehydes is shown mainly by a strong tendency to polymerisation.

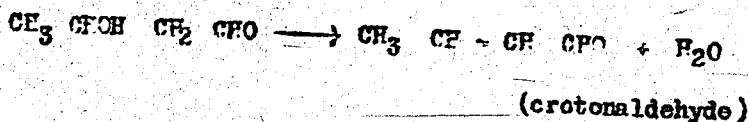
Several low molecular weight aldehydes, as formaldehyde and acetaldehyde combine under the action of acids to stable, non-oxidizable tri-molecular polymeric compounds:



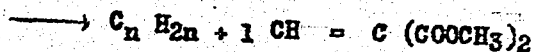
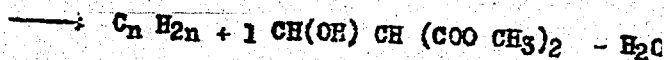
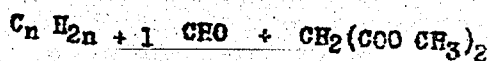
An even more general polymerisation process is the so-called "aldolcondensation". The aldol condensation takes place as follows: the hydrogen atom which belongs to the carbon atom next to the aldehyde group adds on to the oxygen of the other aldehyde group and at the same time the two aldehyde molecules combine with one other by means of a C - linkage to give a double molecule



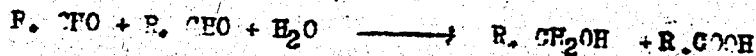
These oxyaldehydes are unstable and decompose once more to give water and unsaturated aldehydes:



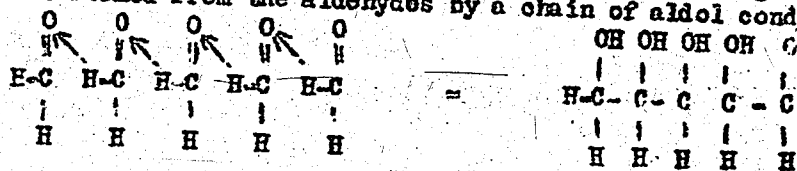
Ethylene compounds also combine with aldehydes, as follows:



Under the action of alkalis an intermolecular displacement of the oxygen takes place for some aldehydes; one half of the aldehyde molecule is reduced, the other half is oxidised to the acid; this is the so-called Cannizzare reaction:



The most noteworthy aldehyde polymerisation is the formaldehyde condensation which gives a quantity of different sugars. These sugars are formed from the aldehydes by a chain of aldol condensations



These are syrupy sugar compounds which represent gums.

This reactivity of the aldehydes is in many cases harmful to the engine; small amounts of aldol condensation products in the fuel behave like gums, i.e. they lead to residue formation.

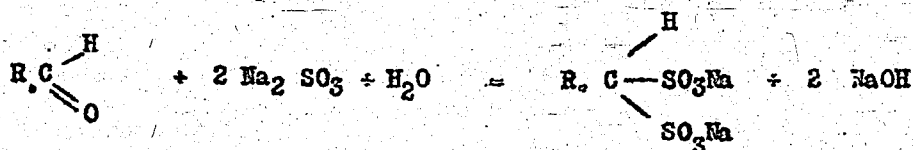
Therefore care has to be taken that aldehydes are not formed in the fuel or only stable aldehydes.

It is important to formulate a quantitative expression for the aldehydes in order to control the manifold reaction possibilities to some extent by means of chemical additive.

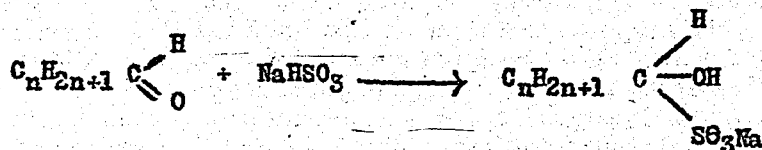
III. Processes for the Quantitative Determination of Aldehydes.

From the many chemical reactions of the aldehydes it appears that sufficient possible means exist for the quantitative determination of the $\text{C}=\text{O}$ group. On the other hand just on this account difficulties arise when carrying out a quantitative determination of the aldehydes in gasoline and it is difficult to separate the different aldehydes from one another. Further also the separation or destruction of the peroxides, which interfere during the determination of aldehydes in fuels, is very difficult.

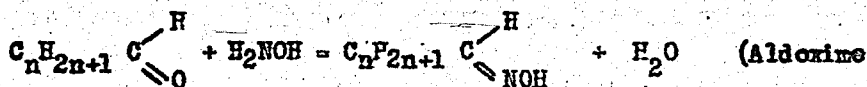
1. Known Processes for Aldehyde Determination: The old process of S.S. Sadtler 2) carries out the aldehyde determination with sodium sulphite. The reaction is illustrated by the following equation:



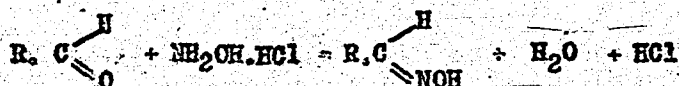
One of the well-known reactions occurs by addition of sodium bisulphite to the aldehydes. In most cases good crystalline precipitates, which are difficult to dissolve, are formed; these can be decomposed into the aldehydes again by dilute acids and alkalis. These reactions are used to separate the aldehydes from mixtures and to prepare them in the pure state. This is represented by the following equation:



The bisulphite addition compounds are in general considered as α -oxisulphonic acids. Very important are the reactions of aldehydes with nitrogen containing reagents, e.g. hydroxylamine, hydrazine, phenylhydrazine and semicarbazide. In many cases sparingly soluble crystalline derivatives are formed which can be employed to identify the aldehydes, to separate them from mixtures and to purify them. The reaction with hydroxylamine gives aldoximes:

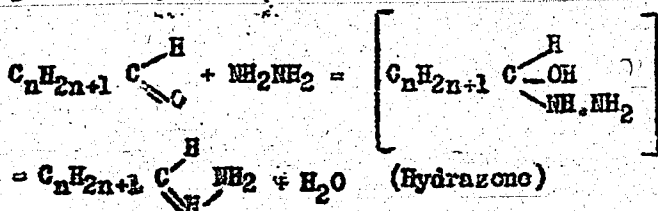


The experiments of A. Reclair and R. Frank³⁾ on the determination of carbonyl compounds were carried out on this basis; by means of hydroxylamine hydrochloride experiments were in the first place carried out on citral and citromellal. This estimation is likewise based on the formation of oximes and titrating the liberated hydrochloric acid, e.g.

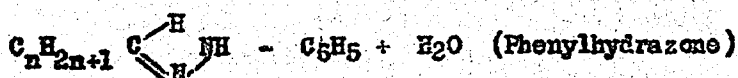


It was noted that the time required for the completion of the experiment varied with the substance to be examined. The aliphatic and aromatic aldehydes according to the authors³⁾ mentioned have roughly the same reaction velocities. The time of reaction is apparently influenced by the spacial arrangement of the molecule. Thus Carvon reacts very slowly, tetrahydrocarvon about as quickly as an aliphatic ketone, fenchon on the other hand does not react at all under technical conditions. In the opinion of the research worker the organic acids must not be neutralised before aldehyde determination, as the hydroxylamine is liberated by alkali salts formed which react with the hydrochloric acid; thus not all the hydrochloric acid is available for the titration.

Aldehyde and hydrazine likewise give a hydrazone, phenyl hydrazine gives phenyl hydrazones:

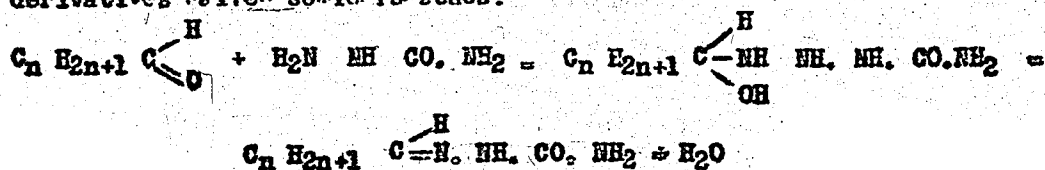


or correspondingly:

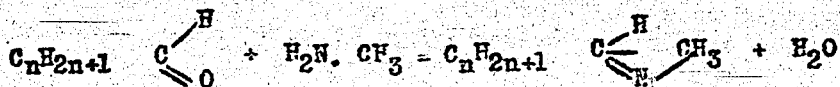


A. Bitel and G. Look⁴⁾ determined aromatic aldehydes by this means. 2,4 dinitrophenylhydrazine was used as reagent, by dissolving 2.5 gm. in 50 cu.m. of concentrated sulphuric acid and diluting this with 950 cu.m. of water. For example, benzaldehyde was dissolved in acid free alcohol and was added to a solution of 2,4 dinitrophenyl hydrazine; this was diluted with water, stirred and the resulting precipitate filtered off. Finally this was washed with sulphuric acid and water and dried at 110°C. o., m and p chlorobenzaldehyde are determined in the same manner.

The very reactive semicarbazide $H_2N \cdot NH \cdot CO \cdot NH_2$ and thiosemicarbazide $H_2N \cdot NH \cdot CS \cdot NH_2$ are often used in the preparation of sparingly soluble aldehyde derivatives called semicarbazones:



Aliphatic amines react with aldehydes according to the same principle:

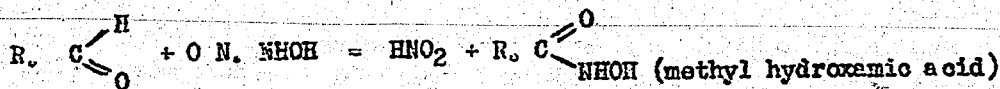


This determination was in effect carried out by W.C. Tobie 5)

Another important proof for aldehydes consists in the latter colouring fuchsin sulphurous acid red: K. Fischbeck and L. Neundorfer 6) worked out a calorimetric method with fuchsin sulphurous acid for the determination of aliphatic aldehydes.

The measurements were carried out by Zeiss in the grade photometer by using the blue S47 filter. Corresponding experiments showed that the instability of the fuchsin sulphurous acid is not due to loss of acid but to the action of atmospheric oxygen; fuchsin sulphurous acid kept under hydrogen remains stable for a long time.

Another reaction for the determination of aldehydes was devised by Angeli Pimini 7) Aldehydes react with nitrohydroxylamine $NO_2 \cdot NHOH$ to give alkylhydroxamic acids; these with $FeCl_3$ give an intensive red coloration, which is easily recognisable:



reference has to be made to the special method of Tauma Veitala 8) for the aldehyde determination. The reduction of the α -bromine atom in α, γ, δ -tri-bromomethon by means of KI in an acid solution to γ, δ -dibromomethon = (2,6 - dibromo 1,1 dimethyl cyclohexane, 3,5-dione) was carried out. On addition of an approximately 50% aqueous alcoholic solution of the aldehyde to the γ, δ -dibromomethon a decrease in the volume would result within several minutes, owing to the interaction between 2 mols. of dibromomethon and 1 mol. of aldehyde. As α -alkyl derivatives of methon do not condense with aldehydes it was surprising to find that α -monobromomethon condensed with aldehydes.

V. Stern and S. Polak 9) suggest the polarographic analysis of mixtures of aldehydes and peroxides. It was found that acids and alkalis are unsuitable as solvents, or as electrolytes because aldehydes cannot be reduced in acid solution and in alkaline solution the reduction potential is displaced to -2.3V, i.e. near that of the reduction potential of the sodium ion. Of other electrolytes, such as $LiCl$, $NaCl$ and NH_4Cl only $LiCl$ is suitable, as in the case of $NaCl$ and NH_4Cl the position is the same for the reduction potential of the cation as for sodium hydroxide. The oxygen dissolved in the electrolyte has to be removed.

A.A. Dobrinaja and L.B. Neumann 10) also support with their experiments the suitability of the polarographic method for the determination of a mixture of aldehydes and peroxides.

2. The application of individual processes for aldehydes

Determination in fuels: With respect to the aldehyde determination in fuels it has to be pointed out that the carbonyl groups $>C=O$ is the active constituent in the $-C \begin{smallmatrix} H \\ \diagup \\ \diagdown \\ O \end{smallmatrix}$ group and thus ketones are included in the investigation of aldehydes in ketones.

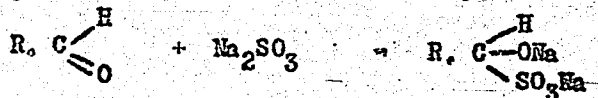
For the aldehyde determination of S.S. Sadtler²⁾ neutral sulphite is used, two molecules of which react with one molecule of the aldehyde. The NaOH liberated is titrated with N/10 hydrochloric acid using thymolphthalein or rosolic acid as indicator. The liquids to be examined have to be neutralised to the indicator.

After several experiments the following procedure was adopted.

10 cu. cm. of the fuel to be examined are mixed with 25 cu. cm. of 2% sodium sulphite and the resulting soda lye is titrated against N/10 HCl. A thymolphthalein solution containing 0.1 weight % thymolphthalein in 90% alcohol is used as indicator. The quantity of N/10 HCl used, expressed in cu. cms, multiplied by 1.45 gives the weight of aldehyde (CHO) in 10 cu. cm of fuel.

This method refers to an aldehyde content of about 20 mg. of the latter in 10 cu. cm fuel. The amounts of reagent used are adjusted in proportion to the aldehyde content.

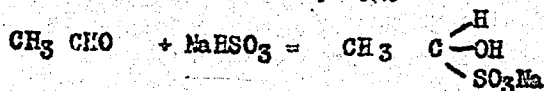
The values shown in table 1 indicate that the sulphite process for the aldehyde determination in fuels gives much too low values. It appears that apart from the reaction indicated above the following side reaction takes place:



As will be shown later, a similar reaction takes place during the conversion of aldehydes with sodium bisulphite. A further difficulty is that the colour change is not well defined in the presence of benzene. The tests carried out with benzaldehyde were completely negative. Here no reaction takes place to begin with, because the indicator thymolphthalein shows no blue colouration. The same behaviour was shown by vanillin already in an aqueous solution.

Thereafter the tests with sodium sulphite were soon given up, as a general application for the quantitative determination of the aldehyde group does not seem possible with this method.

The aldehydes combine also with alkaline bisulphites to give crystalline compounds, e.g.



These compounds are very stable in aqueous solution and the bisulphite thus combined cannot be oxidised by means of iodine. According to Ripper 11) if an aqueous solution of the aldehyde is mixed with an excess of alkaline bisulphite solution of known concentration and the bisulphite which has not combined is determined after a certain time, the quantity of aldehyde present can be evaluated from the amount of bisulphite used up. In the practical tests the aldehyde solution to be tested was placed into an iodine - number flask and mixed with 5 to 10 times the excess of sodium bisulphite; the

unused sodium bisulphite was back titrated with $n/10$ iodine. The following experimental procedure was adopted: 10 cc. of the solution to be examined is mixed with 5 cc of approximately $n/6$ sodium bisulphite solution and the mixture shaken for 20 to 40 mins. in the presence of nitrogen. The unused NaHSO_3 is back titrated with an aqueous or alcoholic solution of $n/10$ iodine - potassium iodide solution.

From the difference in the titration figures obtained with 5 cc. of sodium bisulphite before and after reaction with the aldehyde the amount of $n/10$ NaHSO_3 required for the aldehyde under examination is calculated.

The amount of $n/10$ NaHSO_3 , multiplied by 1.45 gives the amount of aldehyde present in 10 cc. of fuel.

Next propylaldehyde in an alcoholic solution was tested. Table 2 shows the results. The aldehyde values increase with the time taken for shaking the samples. The same was experienced both for aliphatic and for aromatic aldehydes, e.g. benzaldehyde Table 3.

Testing mixed aldehydes in alcohol similarly gives no consistent results. Again the aldehyde value increases with the time of shaking. Table 4.

In the presence of gasoline the aldehyde values are lower throughout, as shown by Table 5. Increasing the time of shaking however the aldehyde values increase again. The increase in the value with the time of shaking is definitely reducible to the oxidation of the bisulphite. For this reason nitrogen was always led into the samples under test. Again variations occurred, which probably were due to more or less sulphur dioxide being expelled from the bisulphite. However working in an atmosphere of nitrogen is preferable to the oxidation of the bisulphite.

Generally speaking however the bisulphite process is not satisfactory as the values obtained in a solution of benzene are not accurate.

Further experiments were carried out with dinitrophenylhydrazine 4) Aldehyde combines with dinitrophenylhydrazine - as already mentioned - to give hydrazones, which are determined gravimetrically in the form of crystalline precipitates.

Unfortunately, however, only aromatic aldehydes can be determined by means of this reagent. The results are indicated by Table 6. Test with aliphatic aldehydes were unsuccessful, as products resulted which were liquid at room temperature or easily attained the melting point when dried. As shown for butylaldehyde in Table 6 - aliphatic aldehydes are found to be too low.

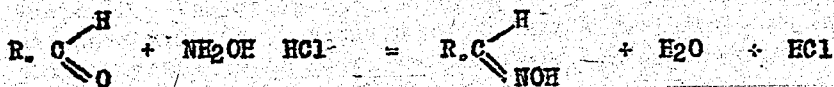
As the aldehyde determination with dinitrophenylhydrazine is not generally applicable an attempt was carried out to oxidise the aldehydes with hydrogen peroxide and determine the resulting acids volumetrically. This oxidation was only partly successful even though the tests were carried out under varying experimental conditions.

Several tests with fuchsin sulphurous acid 6) were in agreement with the experience of G. Damköler and W. Eggersgluss 12) that only in a very narrow range was there a connection between the colour toning and the concentration.

Tests with hydroxylamine hydrochloride to start with brought bad results. These were carried out in an alcoholic solution and the colour change with the indicator methyl orange was not sharp. Only later experiments in very dilute alcoholic solution brought better results. This method was employed mainly for the quantitative determination in fuels, as conversion took place both for aliphatic and for aromatic aldehydes with hydroxylamine hydrochloride.

5. Aldehyde Determination with Hydroxylamine Hydrochloride:

The aldehyde determination with hydroxylamine hydrochloride is based on the reaction:



An oxime, water and hydrochloric acid are formed. The hydrochloric acid formed is titrated with caustic soda. First of all tests were carried out with hydroxylamine hydrochloride to determine the conditions for the quantitative estimation of the aldehydes in fuels. The following points have to be observed.

- 1) Hydroxylamine hydrochloride has to be present in a given excess.
- 2) The tests must not be carried out in an alcoholic solution, as the end-point for methyl orange is not sharp in alcoholic solution. If an alcoholic solution of the aldehyde is used it is necessary to dilute with water strongly.
- 3) The reactivity of the aldehydes varies in general aromatic aldehydes react more slowly than aliphatic aldehydes. It is thus necessary to leave the products of the reaction standing for some time or to shake for a short time.
- 4) It is often necessary to use a comparison solution in order to determine the correct end point.
- 5) Temperatures higher than 20°C should be avoided for the determination of aldehydes by means of hydroxylamine hydrochloride.

After some experimentation the following method was worked out.

To 10 cc of fuel 25 cc of a 0.3% hydroxylamine hydrochloride are added; this mixture is shaken for 15 minutes or is allowed to stand for 15 minutes; the resulting hydrochloric acid is titrated with n/10 NaOH. After a blank determination, i.e. after determining the amount of n/10 KOH required for the hydroxylamine hydrochloride alone, the amount actually required for the aldehyde under test can be calculated. The amount of n/10 KOH used, expressed in cc. and multiplied by 2.9 gives in mg. the amount of aldehyde present in 10 cc. of fuel. In so far as only traces of the aldehydes are present diluted standard solution of KOH leave to be employed.

Next fuels with known amounts of butyl and benzaldehyde are mixed and the aldehydes are determined according to the method described. Tables 7 and 8 indicate the results. In spite of the different treatment for all fuels 91 to 93% by weight of the theoretical butyl aldehyde content present is found. The rest consists - as will be shown later - mainly of acids and products which are formed between benzene hydrocarbons and aldehydes. The reaction takes slightly longer for benzaldehyde, (Table 8) which is shown by the fact that carrying out the titration immediately after mixing low aldehyde values are found.

The reproducibility of the benzaldehyde values is good for the same fuel, however becomes worse if the comparison is made for different fuels, even though the basic fuels indicated in Table 8 contain no aldehydes.

As different aldehydes can be present in the fuels, a mixture of propyl, butyl and benzaldehyde was examined in the presence of Leuna - gasoline, primary and Roumanian gasoline. As seen from Table 9 a complete transformation of the aldehydes by means of hydroxylamine hydrochloride results in most cases. It is again noted that when titration is carried out immediately too low aldehyde values are obtained; otherwise the reproducibility for the same fuel is good. The enhanced period of reaction is reducible to the presence of the benzaldehyde. Table 9 shows further that for primary gasoline too high

aldehyde values are found. This is reducible to the aldehyde present in the basic fuel. Primary benzene contains 5.05 mg. aldehyde in 10 cc. of fuel. Table 10. The other fuels examined are free from aldehydes. After allowance has been made for the basic aldehydes comparable values are obtained with primary gasoline to Leuna gasoline and Roumanian gasoline (of the values indicated in brackets in Table 9).

IV. Determination of Aldehydes in the Presence of Acids and Peroxides.

In actual fact the determination of aldehydes in fuels by means of hydroxylamine hydrochloride gives no difficulties unless other oxidation products, as e.g. organic acids and peroxides are present at the same time.

Above it has been referred to that aldehydes are often unstable. This instability is apparent especially in the presence of certain hydrocarbons, which is confirmed by the following tests.

It was tested to what extent atmospheric oxygen or oxygen present in the fuel influences the acid-formation of aldehyde containing fuels. For this purpose the acid content of butyl aldehyde and benzaldehyde alone was determined. At the same time the acid content in mixtures of gasoline and butyl and benzaldehyde was determined; the fuels used were free from acid. In Table 11 the acid values are collected. The acid contained in butylaldehyde and benzaldehyde on the average amounts to 1.61 to 14.34 weight per cent. The acid content remains the same for butyl aldehyde in the presence of Roumanian gasoline, however increases in the presence of Leuna gasoline and especially in that of Eichstoff Z, where it amounts to 25.45 weight per cent. The aldehyde content for a mixture of Eichstoff Z + 42.9 mg. butylaldehyde, after standing fell to 77.76 weight per cent in contrast to former values which explains the high acid content.

For benzaldehyde smaller differences occur in the acid formation. The highest acid content with 19.63 weight per cent occurs for benzaldehyde in the presence of Leuna - gasoline. It is understood that this sample contains only 82.01 weight per cent aldehyde.

Several of the samples shown in Table 11 do not give 100% by weight if the amount of aldehyde and the amount of acid present are added up. In these cases it is supposed that certain combinations take place between the hydrocarbons present in the fuel and the aldehydes. These compounds are still further investigated at present. Very thorough tests with sodium bisulphite for the determination of aldehydes in the presence of peroxides were unsuccessful. Partly, the sodium bisulphite is oxidised by the peroxides so that a too high aldehyde value is obtained; and partly the peroxides liberate iodine from the iodine-potassium iodide solution, which brings about a too low aldehyde value.

Corresponding tests are being carried out with hydroxylamine hydrochloride. Certain peroxides under definite experimental conditions do not influence the hydroxylamine hydrochloride solution.

V. Summary

It is known that fuels tend to knock more or less and also differential to gum formation - this depending on their chemical composition. The knocking of the fuel and similarly gum formation depends on the tendency of combination of the oxygen atom or molecule with the hydrocarbons present in the fuel, resulting in oxidation product like peroxides, aldehydes, ketones, hydroxides and acids. Whilst in some cases the peroxides strongly lower the anti-knock value, aldehydes are somewhat effective only in the presence of lead tetraethyl. They influence residue formation unfavourably.

For the determination of these oxidation products which are present in the fuels special methods will have to be worked out. Tests on peroxides determination have already been carried out (1 and 15)

In the present report only the determination of aldehydes in the presence of fuels was described. The methods proposed for aldehyde determination were sifted and collected from the literature available. At the same time detailed experiments were carried out to determine aliphatic as well as aromatic aldehydes in fuels.

With sodium sulphite and sodium bisulphite especially in gasoline solution difficulties arose, which prevent accurate aldehyde values being obtained. With dinitrophenyl hydrazine only aromatic aldehydes can be determined quantitatively. The oxidation with hydrogen peroxide was incomplete both with aliphatic and with aromatic aldehydes.

The best results were obtained with hydroxylamine hydrochloride according to the method worked out. With this reagent a general application was possible, so that the aldehydes present in the fuel are determined as the $\text{-C}^{\text{H}}_{\text{O}}$ group.

As hydroxylamine hydrochloride refers to the >C=O group, aldehydes and ketones are evaluated as a sum of the two.

Experiments are still being carried out on the determination of aldehydes in the presence of peroxides.

TABLE I

Determination of Butylaldehyde with Sodium Sulphate

The amount of butylaldehyde in 10 cu.cm. of fuel. mg.	Solvent	Treatment (Indicator thymol-phthalein)	The amount of n/10 HCl used cu. cm.	The amount of butylaldehyde found	
				mg.	weight %
16.63	Alcohol	titrated immediately	1.97	7.1	42.7
16.63	"	allowed to stand for 15 mins.	2.0	7.1	43.33
16.63	"	shaken for 15 mins.	1.99	7.17	43.11
41.8	"	shaken for 15 mins.	4.9	17.6	42.2
41.8	"	shaken for 30 mins.	4.7	16.9	40.51
17.61	Leuna Gasoline	titrated immediately	2.09	7.53	42.76
17.61	"	allowed to stand for 15 mins.	2.14	7.71	43.78
17.61	"	shaken for 30 mins.	2.04	7.35	41.74
20.9	"	titrated immediately	2.46	8.88	42.41
20.9	"	shaken for 15 mins.	2.40	8.65	41.38
20.9	"	shaken for 30 mins.	2.24	8.07	38.6

TABLE 2.

Determination of propylaldehyde with NaHSO_3 (Sodium bisulphite)

10 cu.cm. alcoholic solution employed; amount of propyl- aldehyde. mg.	Treatment in atmosphere of nitrogen.	Amount of n/10 NaHSO_3 used.	Amount of propylaldehyde found	
			mg.	weight %
4.02	Shaken for 5 mins	0.92	2.67	66.42
4.02	Shaken for 5 mins	0.93	2.70	67.16
4.02	Shaken for 10 mins	0.95	2.76	68.65
4.02	Shaken for 10 mins	0.96	2.79	69.65
4.02	Shaken for 20 mins	1.10	3.19	79.35
4.02	Shaken for 20 mins	1.11	3.22	80.10
4.02	Shaken for 40 mins.	1.28	3.72	92.54
4.02	Shaken for 40 mins	1.29	3.75	93.28
4.02	Shaken for 40 mins	1.30	3.77	93.78
4.02	Shaken for 40 mins	1.32	3.83	95.27

TABLE 3.

Determination of benzaldehyde with sodium bisulphite

Amount of alcoholic solution used. 10 cc., amount of benzaldehyde mg.	Treatment in atmosphere of nitrogen.		Amount of $\frac{n}{10}$ NaHSO_3	Amount of benzaldehyde determined	
				mg.	weight %
4.19	Shaken for	1 min.	0.32	1.70	40.57
4.19	"	1 min.	0.32	1.70	40.57
4.19	"	1 min.	0.36	1.91	45.59
4.19	"	1 min.	0.40	2.12	50.6
4.19	"	1 min.	0.41	2.17	51.79
4.19	"	1 min.	0.55	2.92	69.69
4.19	Shaken for	5 min.	0.50	2.65	63.25
4.19	"	5 min.	0.51	2.71	64.68
4.19	"	5 min.	0.55	2.92	69.69
4.19	Shaken for	10 min.	0.60	3.18	75.90
4.19	"	10 min.	0.62	3.29	78.52
4.19	"	10 min.	0.63	3.34	79.71
4.19	"	10 min.	0.68	3.61	86.16
4.19	Shaken for	30 min.	0.75	3.98	94.99
4.19	"	30 min.	0.65	3.45	82.34
4.19	"	30 min.	0.70	3.71	88.54
4.19	"	30 min.	0.69	3.66	87.35
4.19	Shaken for	40 min.	0.75	3.98	94.99
4.19	"	40 min.	0.78	4.14	98.81
4.19	"	40 min.	0.8	4.24	101.19
4.19	"	40 min.	0.75	3.98	94.99

TABLE 4.

Determination of Aldehyde Mixtures with Sodium Bisulphite

10 cc. alcohol solution used; mixture of aldehydes present mg.	Amount of n/5 NaHSO ₃ given.	Determination in an atmosphere of nitro- gen.	Amount of n/10 NaHSO ₃ used.	Amount of mixed aldehydes found	
				mg.	Weight%
2.5	5	Shaken for 10 mins.	0.945	1.37	54.81
2.5	5	" 10 mins.	0.97	1.40	56.25
2.5	5	Shaken for 20 mins.	1.22	1.77	70.8
2.5	5	" 20 mins.	1.24	1.80	72.00
2.5	5	Shaken for 30 mins.	1.41	2.04	81.60
2.5	5	" 30 mins.	1.41	2.04	81.60
2.5	5	" 30 mins.	1.38	2.00	80.00
2.5	2.5	Shaken 40 mins.	0.96	1.39	55.60
2.5	2.5	" 40 mins.	0.95	1.38	55.20
2.5	5	" 40 mins.	1.46	2.12	84.80
2.5	5	" 40 mins.	1.48	2.15	86.00
2.5	5	Shaken 50 mins.	1.50	2.18	87.20
2.5	5	" 50 mins.	1.51	2.19	87.60
2.5	5	" 50 mins.	1.52	2.20	88.00
2.5	5	Shaken for 60 mins.	1.65	2.39	95.60
2.5	5	" 60 mins.	1.66	2.41	96.40
2.5	5	" 60 mins.	1.66	2.41	96.40

TABLE 5

Determination of Aldehydes in Leuna Gasoline with Sodium Bisulphite

10 cc. Leuna Gasoline Amount used mg.	Aldehyde used.	Determination in an atmosphere of nitrogen.	n/10 NaFSO ₃ used	Amount found	
				mg.	weight %
38.39	Butyl-aldehyde	titrated immediately	8.09	29.15	75.93
38.39	"	Shaken for 15 min.	8.11	29.22	76.11
38.39	"	Shaken for 30 min.	8.03	28.93	75.35
38.39	"	Shaken for 50 min.	8.89	32.03	83.43
16.68	Benz-aldehyde	titrated immediately	1.62	8.59	51.49
16.68	"	Shaken for 15 min.	1.70	9.0	53.89
16.68	"	Shaken for 30 min.	2.07	10.98	65.82
16.68	"	Shaken for 50 min.	2.17	11.51	69.06

TABLE 6

Determination of Aldehydes by means of dinitro-phenylhydrazine

Amount used 10 cc. Amount of aldehyde mg.	Aldehyde used.	Solvent	Amount found	
			mg.	weight %
4.19	Benzaldehyde	Alcohol	4.15	98.77
4.19	"	"	4.21	99.52
8.38	"	"	8.25	98.45
8.38	"	Gasoline Alc. (1:1)	7.97	95.1
8.38	"	" (1:1)	8.12	96.9
8.42	Butylaldehyde	Alcohol	7.0	83.13
8.42	"	"	6.97	82.81
8.42	"	Gasoline Alc. (1:1)	5.56	66.06
8.42	"	" (1:1)	6.17	73.16

TABLE 7

Determination of Butylaldehyde in fuels by means of hydroxylamine hydrochloride

10 cc used amount butylaldehyde mg.	Solvent	Determination (Indicator Meth. Orange)	n/10 KOH in cu. cm.	Amount butylaldehyde used.	
				mg.	weight %
42.9	Eichstoff Z	Shaken for 15 min.	5.41	38.98	90.85
42.9	"	" 15 min.	5.48	39.49	92.05
36.7	Leuna Gaso.	titrated immediately	4.72	34.01	92.67
36.7	"	Shaken for 15 min.	4.67	33.65	91.69
42.5	Roun Gaso.	Shaken for 15 min.	5.41	38.98	91.72
42.5	"	titrated immediately	5.45	39.27	92.40
4.84	Leuna Gaso.	" "	0.62	4.47	92.35
9.91	"	" "	1.26	9.11	91.9
18.35	"	" "	2.36	17.0	92.64

TABLE 8

Determination of Benzaldehyde in fuels by means of hydroxylamine hydrochloride

10 cc. used amount of benzaldehyde mg.	Solvent	Determination (Indicator Meth. orange).	n/10 KOH in cu. cm.	Amount of benzaldehyde used.	
				mg.	weight %
24.2	Eichstoff Z	Shaken for 15 mins.	2.11	22.37	92.44
48.4	"	" " 15 mins.	4.16	44.1	91.11
47.95	IG. Eichgaso.	" " 15 mins.	4.36	46.24	96.43
48.3	Leuna gaso.	" " 15 mins.	4.41	46.77	96.83
24.15	" "	Allow. to stand 15 mins.	2.23	23.65	97.93
53.3	Roun. gaso.	Shaken for 15 mins.	4.79	50.80	95.31
26.65	" "	Allow. to stand 15 mins.	2.34	24.82	93.13
10.48	Eichstoff Z	" " " 15 "	0.92	9.76	93.13
9.92	" "	titrated immediately	0.71	7.53	76.00
39.7	" "	" " "	2.92	30.97	78.01

TABLE 9.

Determination of aldehyde mixtures (propyl, butyl, and benzaldehyde) in fuels with hydroxyl-amine hydrochloride.

10 cc used: mixture of aldehyde present in mg.	Solvent.	Determination (Indicator - Meth. Oringo.)	n/10 KOH used cu. cm.	Amount of aldehyde found	
				mg.	weight %
30.13	Leuna Gaso.	Shaken for 15 mins.	9.4	27.26	90.48
30.13	"	Allowed to stand 15 mins.	9.35	27.12	90.01
15.18	"	titrated immediately	4.44	12.88	84.85
30.13	"	Allowed to stand 15 mins.	9.31	27.00	89.61
30.13	"	" " " 30 mins.	9.43	27.35	90.77
12.31	Roum. Gaso.	" " " 30 mins.	3.95	11.46	93.10
12.77	"	Shaken for 15 mins.	4.16	12.06	94.44
13.68	"	Allowed to stand 15 mins.	4.24	12.30	89.91
13.75	Primary Gaso.	Shaken for 30 mins.	6.13	17.78	129.31 (92.44)
13.75	"	Shaken for 15 mins.	6.14	17.81	129.52 (92.66)
13.75	"	Allowed to stand 15 mins.	6.12	17.75	129.09 (92.4)

TABLE 10

Aldehyde Determination in Basic Fuels with
Hydroxylamine hydrochloride.

Name of Fuel.	Amount Used cu. cm.	n/10 KOH used cu. cm.	Amount found Aldehyde + Ketone mg.
Leuna Gasoline	10	0.01	0
I.G. Eichgasoline	10	0	0
Primary Gasoline	10	1.74	5.05
Roumanian Gasoline	10	0.02	0
Pure Benzol	10	0.01	0
Normal Benzene	10	0	0
Eichstoff Z	10	0.02	0
B4 Fuel	10	0.02	0
C3 Fuel	10	0.02	0

TABLE 11

Determination of Organic Acids and Aldehydes in
Fuels.

Sample	Butyric acid or benzoic acid weight %	Amount of butyl aldehyde or benzaldehyde found	
		mg.	weight %
Butylaldehyde	1.62 1.60 1.61	-	-
Benzaldehyde	14.13 14.54 14.34	-	-
Roumanian Gasoline + 42.5 mg. butylaldehyde	1.65	40.68	95.72
Roumanian Gasoline + 53.3 mg. Benzaldehyde	11.0	46.36	86.97
Eichstoff Z + 42.9 mg. Butylaldehyde	25.45	33.36	77.76
Eichstoff Z + 50.8 mg. Benzaldehyde	13.94	42.44	85.55
Leuna Gasoline + 36.7 mg. Butylaldehyde	2.64	32.46	88.46
Leuna Gasoline + 39.7 mg. Benzaldehyde	19.63	32.56	82.01

VI. Literature

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Figure 1. Influence of butylaldehyde upon the anti-knock value of lead containing and lead-free Leuna-gasoline.

Figure 2. Influence of benzaldehyde upon the anti-knock value of lead containing and lead free Leuna-gasoline.