

Report 8925

RECOVERY OF HYDROGEN PEROXIDE FROM
"PROPANE PEROXIDES"

P. L. Kooijman

Frames 2595-2640

TranslationSUMMARY AND CONCLUSIONS

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In this report is described an investigation of the recovery of hydrogen peroxide from "propane peroxides". This investigation has been in progress since June, 1940.

In the first part of the report is given a summary of a single selective solvent test in which it was attempted to contact the combustion gases from propane peroxide preparation with a solvent that would selectively extract either the hydrogen peroxide or the aldehydes. These tests did not lead to the desired result, but offered an inducement to go on to further investigations in which a propane peroxide solution was vacuum distilled in the presence of salts (Part 2). The latter tests gave good results. We obtained an aqueous, aldehyde-free solution of hydrogen peroxide containing organic acid (formic). This process is not, however, entirely free from explosion hazards.

It was further found that, during the distillation, the organic peroxides decomposed selectively to form formic acid. The hydrogen peroxide decomposed only slightly.

In the third part is described an experiment in which an attempt was made to remove the formic acid by a preliminary decomposition comprising distilling the peroxide solution under vacuum. Explosion was avoided by the constant addition of water. This method was improved by passing steam through a rectifying column countercurrently to the hydrogen peroxide-formic acid solution under such conditions that a formic acid-free solution of hydrogen peroxide was withdrawn from the kettle. These tests showed that the desired objective can be obtained, provided one starts with an uncontaminated solution of formic acid in hydrogen peroxide. When we started with a preliminarily decomposed propane peroxide solution, the formic acid removal appeared to be incomplete, since the decomposition of organic peroxides appeared to be still going on. In order to clarify this matter, the preliminary decomposition of propane peroxides was investigated (Part 4). We found that the preliminarily decomposed propane peroxides still contained organic peroxides. This explanation was expected.

Investigations directed toward improving the selectivity of the

preliminary decomposition (by addition of KCl and by variation of temperature and of concentration) gave no positive results.

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Assuming that the preliminary decomposition might be satisfactory if the formic acid were removed as rapidly as formed in a column in which the down-flowing peroxide solution was contacted with steam, we carried out tests in which the decomposition velocity was determined at 70 and at 90 C.

In these tests, corrections were made for the release of active oxygen which oxidized the formic acid to carbon dioxide. The time necessary for complete removal of organic peroxides at 90 C is considerably more than 2 hours; therefore, the method is not very attractive.

Under the influence of potassium hydroxide, the selectivity of the preliminary decomposition seems to be complete. In this method, however, sufficient potassium hydroxide must be present to neutralize the formic acid formed. Furthermore, it seems that the distillation of the preliminarily decomposed solution substantially without further decomposition is possible if enough sulfuric acid is added to reconvert the potassium formate to formic acid. This method is, however, too expensive.

In conclusion, we may say that, in principle, the recovery of hydrogen peroxide from propane peroxides can be accomplished by several different methods.* Whether a commercially suitable method is available is very dubious.

*See also the method, involving the peroxides of the alkaline earth metals, described in the writer's dissertation. (Delft 1942, p. 72)

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RECOVERY OF HYDROGEN PEROXIDE FROM "PROPANE PEROXIDES"

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INTRODUCTION

In connection with our investigation of peroxides prepared from propane, we have studied the possibility of preparing pure hydrogen peroxide from "propane peroxide" as well as the action on sodium perborate. The preparation has been accomplished by previously described methods (1, 16), which are based on the reaction of the propane peroxides with calcium hydroxide to form calcium peroxide. The calcium peroxide, in aqueous suspension, can be decomposed with carbonic acid to form hydrogen peroxide.

The investigation described in this report was an attempt to recover the hydrogen peroxide directly from the propane peroxides.

This investigation was conducted principally with "synthetic" propane peroxides, i.e. with a solution obtained by mixing hydrogen peroxide and formaldehyde. In the mixture, equilibrium was obtained between formaldehyde and hydrogen peroxide on the one hand and monohydroxymethyl hydroperoxide and dihydroxydimethyl peroxide on the other (10). The experiments in which "true" propane peroxides were used are reported separately.

The experiments described in the third part were carried out with a mixture of hydrogen peroxide and formic acid, since the aim was to separate these compounds. The organic peroxides present in the propane peroxides decomposed to form mainly formic acid. The hydrogen peroxide decomposed only slightly.

PART I

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SELECTIVE WASHING OF COMBUSTION GASES FROM
PROPANE PEROXIDE PREPARATION

As previously reported (2), the peroxides prepared from propane are to be considered as an aqueous solution of hydrogen peroxide and aldehydes, chiefly formaldehyde, in which these compounds are in equilibrium with the condensation products monohydroxyalkylhydroperoxides and dihydroxydialkylperoxides (10).

It is assumed (3, 11) that the hydrogen peroxide and the aldehydes are present in the combustion gases and are uncombined in the vapor phase, so that, upon condensation, in which considerable water is also condensed, these two compounds have an opportunity to interact.

(1) See literature cited at end of this report.

If this assumption is correct, it is theoretically possible to separate the hydrogen peroxide from the aldehydes.

This separation has already been partially accomplished in fractional condensation experiments (4), in which it appeared possible to increase the maximum perborate activity (6) by about 10 units, by conducting the condensation in a water-cooled condenser at 35 C.

In the second separation method described, the combustion gases were passed through a solvent, which was maintained at about 100 C for the purpose of preventing undesired condensation.

The apparatus used comprised a glass wash bottle (Fig. 1) in which the solvent could be maintained at any desired level by the use of compressed air. The solvent could be heated to about 100 C by means of a heating coil. Combustion gases, produced by the oxidation of propane under optimum conditions, were passed through the solvent, and the solvent-treated effluent gases were cooled in an ordinary cooling system. It was expected that the aldehydes or the hydrogen peroxide, depending on the nature of the solvent, would be selectively absorbed by the solvent.

Some of the solvents are listed as follows:

- 1.° Cetane. Hydrogen peroxide does not dissolve. The aldehydes dissolve to some extent. It appeared, however, that nothing remained in the cetane. The condensate separated from the off-gas had the same perborate activity (6) as that from a blank run without a solvent. 2602
- 2.° Sulfuric acid, the concentration of which was so chosen that the partial pressure of the water was equal to that in the combustion gases, was unsuitable because of marked foaming.
- 3.° Phosphoric acid, the concentration of which was chosen in the same way as that of the sulfuric acid, gave no experimental difficulties. Considerable peroxide decomposition was, however, obtained.
- 4.° A saturated aqueous solution of potassium bisulfate seemed, after contact with the combustion gases, to contain active oxygen. In a short experiment, the decomposition of active oxygen compounds was slight. When, however, the experiment is continued for a longer time, the decomposition increases.

According to the "KI velocity curve" (7,12), there appeared to be a certain selectivity in the treatment. The aldehyde-hydrogen peroxide ratio in the enriched solvent was lower than that of the blank condensate. This was the first indication that the desired objective could be attained by such a method.

After this experiment there was considered the idea of vacuum distilling the peroxide-enriched solvent to obtain a material having a considerably higher perborate activity than the blank condensate. By vacuum distillation, we obtained a distillate containing hydrogen peroxide free from organic peroxides.* The distillate did, however, contain an appreciable amount of formic acid. The loss of active oxygen through decomposition was, however, very great, viz. 60 per cent.

- 5.0 A saturated aqueous solution of magnesium perchlorate. This material was used with the intention of preventing the formaldehyde in the combustion gases from going into solution as the hydrate. The formaldehyde should then pass through the solvent as the monomer.

Upon distillation of the enriched solvent thus obtained, which contained 76 per cent of the active oxygen of the combustion gases, we obtained, with very slight loss of active oxygen through decomposition, a distillate that contained hydrogen peroxide and no organic peroxides[†]. 2603

This result led us to conduct a vacuum distillation of a magnesium perchlorate solution to which had been added untreated propane peroxide. The results so obtained were analogous to those of the preceding experiment. It therefore appeared advisable to discontinue the solvent experiments. Since it appeared possible to distill the propane peroxides in vacuo in the presence of magnesium perchlorate without explosion, we continued the investigation in this direction (See Part 2).

PART 2.

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VACUUM DISTILLATION OF PROPANE PEROXIDES IN THE PRESENCE OF SALTS

#1. Orienting Investigation

The isolation of the hydrogen peroxide contained in propane peroxides by vacuum distillation is, in principle, possible. This procedure is, however, not advisable in practice, since the organic peroxides (hydroxy-alkyl peroxides), part of which remain in the kettle, are explosive. Explosion always occurs during distillation.

As mentioned in Part 1, it is possible to distill propane peroxides in the presence of magnesium perchlorate without explosion. Apparently the salt has explosion-inhibiting properties. As previously mentioned, it is possible, by vacuum distillation of a dilute propane peroxide solution to which the salt has been added, to obtain hydrogen peroxide in the distillate

*Determined by use of the "KI velocity curve" (7,12). Determination of the "perborate activity" was impossible because of the low peroxide concentration.

free from aldehydes and organic peroxides.

We have now continued the investigation with the aim of finding a salt which is commercially attractive.

As mentioned in Part 1, the "KI velocity curve" (7, 12) was used to show the substantial absence of organic peroxides in the distillate containing the hydrogen peroxide. When this curve coincided with that obtained with hydrogen peroxide alone, it was safe to assume that no organic peroxide was present in the distillate.

In most cases, we used synthetic propane peroxides, prepared by mixing hydrogen peroxide and formaldehyde, which could be used in the determination of small quantities of formaldehyde or of hydroxyalkyl peroxides in the presence of hydrogen peroxide according to the method of Flank and Finkenbeiner (13). This method is based on the oxidation of formaldehyde to formic acid by hydrogen peroxide in alkaline solution.

The following salts were used in these distillations:

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- 1.° Magnesium perchlorate, which is not commercially suitable, since it has explosive properties itself and is very expensive.
- 2.° Calcium nitrate, which gave desirable results. This salt is also explosive by itself. In fact, an explosion was obtained in one test.

Since, in these distillations, the distillate containing the hydrogen peroxide also contained considerable amounts of formic acid (a product of the decomposition of the hydroxyalkyl peroxides in the charge), we tried to distill in the presence of:

- 3.° Sodium bicarbonate, which can combine with the organic acid formed. Apparently, however, 96 per cent of the active oxygen compounds decomposed during the distillation.
- 4.° Sodium metaphosphate, which is known to stabilize hydrogen peroxide solution, appeared to promote decomposition to a great extent (88 per cent).
- 5.° Finally, the most attractive material seemed to be anhydrous sodium sulfate. Good results were obtained, and no eventual technical difficulties appeared likely.

#2. Experiments with Anhydrous Sodium Sulfate as an Explosion Inhibitor

In the following table, the results of a representative run with sodium sulfate are given:

TABLE 1

Run Q. 12.

Intake, 260 cc solution containing 50 gm Na₂SO₄ and 751 milliequivalents synthetic propane peroxides (pba, 60 %); cooling water at 5 C; pressure, 10-12mm

Fraction	Temp. of Water Bath, C	cc	Total Active O, meq	Total Acid, meq	Aldehyde, mmol/cc	φ**	Calc. (9) pba, %
1	50-42	30.2	7.5	2.18	0.108	0.88	44
2	42-43	30.5	2.3	0.19	0.029	0.76	51
3	43-43	30.2	2.4	0.11	0.018	0.45	70
4	43-44	31.0	2.9	0.19	0.019	0.41	72
5	44-46	30.4	5.6	0.26	0.025	0.27	81
6	48-49	30.3	12.8	0.39	0.025	0.12	90
7	49-51	29.9	14.9	0.53	0.023	0.09	91
8	51-100	29.2	437.5	88.18	0.114	0.02	95½
-80 C***	-	5.8	9.8	45.93			
Resid.	-	-	-	-	-	-	-
Total	-	-	496±	138	-	-	-

*pba = perborate activity (g)
66% of intake

**φ = millimoles aldehyde/millimoles peroxide

*** Collected in trap at -80 C after the condenser.

From these results, it is seen that the last fraction of the distillate (fraction 8) contained 457.5 milliequivalents of peroxide, i.e. 88 per cent of the total amount distilled. The perborate activity of this fraction, calculated from the formaldehyde content, is 95 1/2 per cent; the product is therefore practically pure hydrogen peroxide. The fraction did, however, contain a considerable amount of formic acid.

The total active oxygen yield from the distillate was 66 per cent, which is of about the same order of magnitude as the perborate activity. On further consideration, it did not seem so strange to us that a connection might exist between these two quantities.

In order to trace this connection, we conducted a distillation with synthetic propane peroxide that had a perborate activity of 25 per cent. The results are given in Table 2. In this run, the aldehyde content of the fractions was not determined.

TABLE 2

Distillation C. 14.

Intake, 260 cc of a solution containing 50 gm Na_2SO_4 and 755 milliequivalents synthetic propane peroxides (pha, 23 %); cooling water at 5 C; pressure, 10-20 mm.

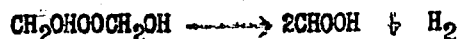
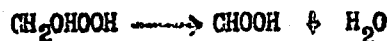
Fraction	Temp Water Bath, C	cc	Total Peroxide, meq	Total Acid, meq
1	28-46	30.2	1.06	3.75
2	46-48	30.3	0.88	1.79
3	46-48	30.2	0.91	1.54
4	46-48	30.4	2.10	1.86
5	48-53	30.4	4.62	3.26
6	53-56	30.2	6.95	3.69
7	56-57	30.7	6.78	5.40
8	57-100	28.0	174.2	227.5
-30 C		10.8		128.3
Res.			25.6	41.44
Total			221 = 30 % of intake	419

The total active oxygen yield from this distillation was 30 per cent, as shown in the table. It is actually somewhat higher than the perborate activity.

From the results obtained up to this point, we must assume that, during distillation, the organic peroxides decompose to form organic acids, whereas the hydrogen peroxide distills over unchanged.

The formic acid must originate from the decomposition of the hydroxyalkyl peroxides in the propane peroxides in accordance with the following equations (9, 10):

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It appears from the results, which were obtained by distillation of a mixture of hydrogen peroxide and formic acid, and from the course of the formic acid concentration in the two distillations mentioned, that the formic acid is formed just at the end of the distillation when the temperature is high. Moreover, this effect must represent a selective decomposition of the organic peroxides.

We desired to follow this selective decomposition of the organic peroxides separately.

For this purpose, a solution of synthetic propane peroxides having a perborate activity of 60 per cent was heated at 80 C in a flask provided with a reflux condenser. The peroxide and the acid content of samples of this solution were determined as a function of time.

The results are shown in Table 3 and in Figure 2.

TABLE 3

Selective Decomposition at 85 C.

Time, min	Peroxide, mmol/cc	%	Acid, mmol/cc	%
0	3.59	100	0	0
24	2.32	65	1.23	57
45	1.86	52	1.56	65

(Continued)

Table 3 (Continued)

Time, min	Peroxide, mmol/cc	%*	Acid mmol/cc	%*
80	1.34	37	1.53	62
120	0.97	27	1.23	57
240	0.64	18	1.10	51

*Based on the amount of formaldehyde originally present.

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From these data, we see that the acid concentration attained a maximum in about 45 minutes. At that moment, about 52 per cent of the original peroxide content is still present. The maximum acid formation results in a concentration of 1.36 millimoles per cc. This value corresponds to an acid yield of 63 per cent, based on the original formaldehyde content.

The decrease of the acid content after 45 minutes was apparently due to the oxidation of the formic acid, by the hydrogen peroxide, to carbon dioxide.

From these experiments, it may be concluded that the organic peroxides decompose more rapidly than hydrogen peroxide. Thus a selective decomposition occurs, as mentioned previously.

After the experiment reported in Table 3, a portion of propane peroxides, previously heated at 85 C for 3/4 hour (preliminarily decomposed), was distilled in the presence of sodium sulfate as described in connection with Experiment Q. 12.

The results are given in Table 4.

TABLE 4

Experiment Q. 16.

Intake, 260 cc of a solution containing 760 meq peroxide (pha, 60%). After preliminary decomposition, 458 meq peroxide was still present.

Fraction	Temp Water Bath, C	cc	Total Peroxide, meq	Total Acid, mmol
1	23-45	30.2	1.5	6.45
2	45-47	30.1	1.7	6.63
3	47-49	30.2	2.1	7.97

(Continued)

Table 4 (Continued)

Fraction	Temp Water Bath, C	cc	Total Peroxide, meq	Total Acid, mmol
4	49-50	30.5	2.4	10.15
5	50-51	30.0	4.8	15.82
6	51-56	31.0	16.0	19.55
7	56-59	29.4	27.9	19.47
8	59-100	28.0	342.2	34.55
-80 C	-	14.5	1.2	1.46
Res	-	-	0	1.60
Total	-	-	400	123

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In this experiment, 55 per cent of the original active oxygen remained intact, and, on account of the preliminary decomposition, the formic acid distribution among the various fractions was similar to that shown in Table 2; the formic acid-peroxide mol ratio in the last fraction was 20 per cent in the present instance and 40 per cent in Table 2.

As a general conclusion from the work reported in this part, it may be said that it is possible to obtain a substantially aldehyde-free solution of hydrogen peroxide by vacuum distillation of propane peroxides in the presence of sodium sulfate as an explosion inhibitor. The solution contains formic acid, the amount of which can be reduced to about half, by the action of the organic peroxides originally present, in a preliminary selective decomposition.

#3. Attempted Removal of Formic Acid from a Preliminarily Decomposed Propane Peroxide Solution by Rectification

In connection with the previously described work, it was important to be able to separate the hydrogen peroxide from the formic acid present in the preliminarily decomposed propane peroxide solutions by rectification. In such a separation, anhydrous sodium sulfate should be used as an explosion inhibitor.

The boiling points of the compounds concerned are as follows at atmospheric pressure:

water	100 C
formic acid azeotrope (22.5 wt per cent water)	107 C (17)
hydrogen peroxide	152 C (14)

Thus the separation of water and formic acid on the one hand and hydrogen peroxide on the other causes no difficulties, provided that the concentration of large quantities of hydrogen peroxide in the kettle causes no trouble.

The apparatus consisted of a Vigreux vacuum column 12 mm in diameter and 2 meters long. The column was provided with a liquid-phase take-off and was estimated to have about 12 theoretical plates. The kettle was heated by means of a water bath.

In the most representative of these experiments, 770 milliequivalents of synthetic propane peroxides (formaldehyde-hydrogen peroxide mol ratio, 0.60; i.e. a pba of 60 per cent) in 350 cc of solution was preliminarily decomposed at 100 C in such a way that about 65 per cent of the active oxygen compounds remained undecomposed. Then 100 grams of anhydrous sodium sulfate was added, and the mixture was distilled until no more formic acid and water came over. The distillate contained a large amount of formic acid and a small amount of active oxygen. 2611

The residue, which contained 486 milliequivalents of active oxygen, was dissolved in 500 cc of water. This solution was distilled in an ordinary distillation apparatus in order to purify the hydrogen peroxide.

The results are summarized in Table 5.

TABLE 5

Fraction	cc	Total Peroxide, mec	Total Acid mmol
1-8	239.3	33.3	4.8
9	29.8	5.3	1.5
10	29.9	27.0	1.9
11	30.2	28.0	1.2
12	29.9	37.6	1.3
13	28.7	70.8	1.5
14	22.0	202.5	3.4
Res	-	32.2	1.4
Total	-	437	17.0

Thus 437 milliequivalents or 70 per cent of the original active oxygen remained intact, whereas the last fraction (No. 14) contained only 3.4 millimoles of formic acid.

From these results, it seemed to us to be possible to realize

the desired recovery of hydrogen peroxide from propane peroxides (15).

The commercial operation of this process, however, is not very attractive, since, in another of these distillations, in spite of the presence of sodium sulfate, an explosion destroyed the entire apparatus. This explosion must evidently be ascribed to the fact that, toward the 2612 end of the distillation, a highly concentrated mixture of hydrogen peroxide and formic acid is present, and these two compounds, in spite of the presence of sodium sulfate, reacted explosively to form carbon dioxide and water.

Part 3.

THE REMOVAL OF FORMIC ACID FROM A PRELIMINARILY DECOMPOSED PROPANE PEROXIDE SOLUTION BY THE USE OF WATER AND OF STEAM

#1. Introduction

In order to eliminate the explosion hazard, we sought a method, not for the removal of formic acid and water, but for distilling over formic acid alone, the aim being always to maintain a dilute solution of hydrogen peroxide in the kettle.

We attained this aim in two different manners, which are identical in principle:

- 1.° By the use of a vacuum distillation column having only about 2 or 3 theoretical plates, whereby a water-formic acid mixture is separated from the hydrogen peroxide and whereby water is continuously supplied to the kettle during the distillation (#2).
- 2.° By contacting a downward-flowing hydrogen peroxide-formic acid solution in a column with an upward-flowing current of steam, so that a hydrogen peroxide solution free from formic acid is collected in the kettle (#3).

#2. By the Use of Water

The apparatus used consisted of a 1/2-liter, round-bottom flask provided with a Vigreux condenser 3 cm in diameter and 70 cm long (2 to 3 theoretical plates) without a condenser. The vapor evolved during vacuum distillation was condensed in a Liebig condenser.

The most notable results are given in Table 6

TABLE 6

<u>Experiment</u>	<u>W. 3</u>	<u>W. 4</u>	<u>W. 5a</u>	<u>W. 5b</u>
Initial H ₂ O ₂ , mmol	392	392	245	203
Initial CHOH, mmol	235	235		

(Continued)

Table 6 (Continued)

Experiment	W. 3	W. 4	W. 5a	W. 5b
Initial CHOOH, mmol	-	-	129	8
Volume solution, cc	84	84	120	100
Na ₂ SO ₄ added, gm	100	-	-	-
Preliminary decomposition temp, C	70	70	-	-
Preliminary decomposition time, min	25	120	-	-
Pressure, mm Hg	40	40	40	40
Distillation time, hr	4 $\frac{1}{2}$	5 $\frac{1}{2}$	5	5
H ₂ O added, cc	850	1090	760	680
Distillate, cc	812	1110	750	555
H ₂ O ₂ in distillate, mmol	28	6	26	3
HCOOH " " " "	118	75	116	5
H ₂ O ₂ in residue, mmol	301	205	206	196
HCOOH " " " "	32	21	8	3
Peroxide decomposition % of total charge	16	42	5	2
Peroxides in residue, % of total charge	77	56	84	97
Peroxides in distillate, % of total charge	7	2	11	1
Moles HCOOH per 100 moles peroxide in kettle	11	10	4	1 $\frac{1}{2}$

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From the first two experiments (W. 3 and W. 4), in which preliminary decomposition time was varied, it is seen that, after about 5 hours of distillation with continuous addition of water, in both experiments, about 10 moles of formic acid per 100 moles of hydrogen peroxide was present in the kettle product.

Since the possibility existed that not all the organic peroxide

was decomposed, we used, in experiment 5, a mixture of hydrogen peroxide and formic acid. After 5 hours of distillation, 4 moles of formic acid per mole of hydrogen peroxide appeared to be present in the kettle product. After 5 additional hours of distillation (5b) only 1 1/2 moles of formic acid per 100 moles of hydrogen peroxide were present. From these experiments, it seems that the supposition that, at the time of distillation, the preliminary decomposition is still going on is justified. 2615

The following conclusion may be drawn from the experiments described above:

It is possible to separate formic acid from a solution containing formic acid and hydrogen peroxide by the method described. Much time is required, however, to eliminate the formic acid completely. Furthermore, the preliminary decomposition continues during the distillation, and, consequently, formic acid is continuously formed in the residue.

#3. By the Use of Steam

In the first series of experiments described in this section (Table 7), the formic acid separation was carried out by countercurrent contacting of the formic acid-containing hydrogen peroxide solution with steam in a distillation column.

At first, a mixture of pure hydrogen peroxide with formic acid was used, whereas later, a preliminarily decomposed propane peroxide solution was used.

The apparatus (Fig. 5) used consisted of a Vigreux column 18 mm in internal diameter and 3 meters long. About 70 cm from the top was an intermediate inlet, provided with a stopcock, through which the hydrogen peroxide solution containing the formic acid was continuously introduced. In the flask (kettle) attached to the bottom of the column and placed in a water bath, was placed, at the beginning of the experiment, a 30 weight per cent solution of hydrogen peroxide. Superheated steam was then passed into this flask.

In conducting the experiments, it was an object to select the operating conditions (pressure, steam rate, charge rate, column heating, bath temperature, etc.) so that the distillate contained only water and formic acid, and so that no formic acid reached the kettle. In addition, it was intended to keep the decomposition of the hydrogen peroxide and the oxidation of the formic acid (to carbon dioxide and water) at a minimum. A pressure of 40 to 50 mm was maintained in order to permit the use of low temperatures.

The introduction of steam was started at the beginning of each experiment. After several minutes, the stopcock on the intermediate inlet was opened and the introduction of the formic acid-hydrogen peroxide solution was begun. After 50 minutes, during which distillate was regularly taken off and hydrogen peroxide was collected in the kettle, the intermediate inlet was closed and steam alone was passed through the apparatus. During the "steaming", the reflux ratio was determined, with the take-off stopcock wide open, by measuring the amount of distillate per minute (a cc per minute). For a distillation rate of b cc per minute 2616

(averaged over the entire experiment) the reflux ratio is then $(a-b)/b$.

After we had conducted a number of experiments with hydrogen peroxide-formic acid mixtures, it seemed that good results were obtained by the combination of a high bath temperature, a high steam rate, and a maximum reflux ratio.

In Table 7, are given the results of some of the most representative experiments (D 8 and D 19). The results of one experiment with a lower steam rate (D 16) and of one with a lower bath temperature (D 8) are given.

TABLE 7

<u>Experiment</u>	<u>D 8</u>	<u>D 16</u>	<u>D 18</u>	<u>D 19</u>	
Pressure, mm Hg	46-48	41-42	41	40-42	
Column heat, amp	2.5-3.5	3.2	3.2	3.2	
Duration, min					
Steam addition	5	5	5	5	
Steam charge addition	50	50	50	50	
Steam addition	3	9	8	10	
Reflux ratio	-	1.4	0.82	0.85	
Temp water bath, C	65	90	90	90	
Charge to kettle, cc 50 % H ₂ O ₂	50	25	25	25	
H ₂ O ₂ in kettle, mmol	485	245	245	245	
Steam rate, total, gm	281	197	276	294	
Steam rate, gm/hr	302	184	272	280	
Intermediate addition, 2d period, cc	60	10	20	30	
Total H ₂ O ₂ charged, mmol	555	61	122	183	
Total HCOOH charged, mmol	144	24	47	72	
Total distillate, cc	517	219	510	336	2617
H ₂ O ₂ in distillate, mmol	219	6	6	10	
H ₂ O ₂ , % of total charge	26	2	2	2	
HCOOH, in distillate mmol	102	12	58	65	

(Continued)

Table 7 (Continued)

<u>Experiment</u>	<u>D 8</u>	<u>D 16</u>	<u>D 18</u>	<u>D 19</u>
HCOOH, % of total added	71	50	81	90
Final kettle product, cc	74	13	11	13
H ₂ O ₂ in kettle product, mmol	650	261	327	391
H ₂ O ₂ , % total peroxides added	77	85	89	92
HCOOH in kettle, mmol	38	5	1	2
HCOOH in kettle, % of total charged	26	21	2	3
H ₂ O ₂ decomn and loss, %	-3	13	9	6
HCOOH " " " "	5	29	17	7

Thus we see that, in experiments D 18 and D 19, only 2 to 3 per cent of the total formic acid reached the kettle.

Experiments with Continuous Withdrawal of Kettle Product

We conducted several experiments in which the kettle product was continuously withdrawn. A narrow tube was fused onto the bottom of the kettle. The tube was provided with a stopcock. It discharged into a calibrated tube which could be evacuated. Kettle product was withdrawn at about 10-minute intervals.

The conditions under which these experiments were conducted were similar to those shown in Table 7 for experiments D 18 and D 19. The results of the most significant experiments are given in Table 8.

In these experiments (CD 4 and CD 6), the starting material was propane peroxides of which about 60 per cent of the active oxygen had been removed by preliminary decomposition. In the preliminary decomposition, about 55 per cent of formic acid, based on the formaldehyde originally present, was formed. The amount of formic acid that got into the kettle product seemed to be considerably higher than in the experiments in which mixtures of hydrogen peroxide and formic acid were used as starting materials (Table 7). Moreover, the perborate activity of the kettle product was very low (72 and 82 per cent, respectively). The selectivity of the preliminary decomposition is apparently incomplete, and further formic acid formation probably occurs in the kettle; hence the negative formic acid losses. (See also #2). 2618

TABLE 8

<u>Experiment</u>	<u>C. D. 4</u>	<u>C. D. 6</u>
Pressure, mm Hg	59.41	59.41
Column heat, amp	3.0	3.0
Duration, min	4114.8	4151.9
Temp water bath, C	92	80
Steam rate, gm/hr	234	235
Reflux ratio	0.76	1.1
Charge		
Peroxide concn. mmol/cc	5.97	5.97
HCOOH concn, mmol/cc	3.58	3.58
Preliminarily-decomposed charge		
Peroxide concn, mmol/cc	3.55	3.74
Acid concn. mmol/cc	2.59	1.96
Yields from preliminary decomposition, %		
Peroxide	59	63
Acid	72	55
Intermediate charge to column		
Vol, cc	74.0	103.4
Peroxide content, mmol	263	387
Acid content, mmol	192	203
Distillate		
Vol, cc	560	720
Peroxide, mmol/cc	0.035	0.056
" , mmol total	19.5	40
Acid, mmol/cc	0.555	0.273

(Continued)

Table 8 (Continued)

<u>Experiment</u>	<u>C. D. 4</u>	<u>C. D. 6</u>
Acid, total	199	196
Kettle product		2619
Vol, cc	5.6	26.0
Peroxide, mmol/cc	21.4	6.07
" , mmol total	119.5	210
Acid, mmol/cc	0.285	0.49
" , mmol total	1.6	12.8
Perborate activity, %	72	82
Rinsings*		
Peroxide, mmol	47.8	74
Acid, mmol	2.65	7.5
Kettle product		284 (74%)
Peroxide, mmol**	167 (61%)	
Acid, mmol**	2.2 (1%)	17 (8%)
Distillate		
Peroxide, mmol**	19.5 (7%)	40 (10%)
Acid, mmol**	199 (104%)	199 (98%)
Losses		
Peroxide, mmol**	76.5 (29%)	63 (16%)
Acid, mmol**	-9.2 (-5%)	-13 (-6%)
Yields		
Total active oxygen %***	58	47
Perborate activity "H ₂ O ₂ ", % ***	46	65
H ₂ O ₂ %***	51	80

* At the end of the experiment, the column hold-up and the peroxides remaining in the kettle were rinsed together. In the yield calculations, the peroxides and the acid were distributed proportionally between the kettle product and the distillate.

** Percentages based on intermediate charge to column.

*** Percentages based on propane peroxides not preliminarily decomposed.

Conclusion

From the results of the experiments described above, it may be concluded that complete recovery of hydrogen peroxide by the method described is not to be expected.

Part 4

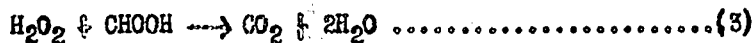
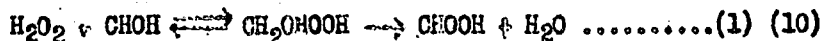
2620

BRIEF INVESTIGATION OF THE PRELIMINARY DECOMPOSITION#1. Introduction

In the work reported in the preceding part, it was found that it is impossible to remove formic acid completely from the preliminarily decomposed propane peroxides, because the preliminary decomposition is not completely selective.

In the work described in Part 2, in which substantially aldehyde-free hydrogen peroxide was obtained by distillation, this seemed not to be the case. We have not yet found an explanation of this difference.

The reactions which might occur during the preliminary decomposition are:



If we started with a mixture of 100 moles of water and 60 moles of CHOH ($\rho = 0.60$) and the entire preliminary decomposition proceeded according to reaction 1 or 2, we could expect the following results:

Reaction	H ₂ O ₂	CHOH	H ₂ O ₂ Remaining	CHOH Formed
(1)	100	60	40	60
(2)	100	60	70	60

In the preliminary decomposition, it appears that 60 to 70 per cent of the active oxygen remains undecomposed. Considering the fact that reactions 3 and 4 also certainly occur, one may draw the temporary conclusion that the selective decomposition is incomplete and that therefore

organic peroxides are always present in the preliminarily decomposed propane peroxides.

This is the hypothesis on which we based our further study of the preliminary decomposition. Moreover, we sought means to improve the selectivity.

#2. Examination of Preliminarily Decomposed Propane Peroxides

The most suitable method for learning more about the preliminary decomposition seemed to be to determine the carbon and acid contents of the preliminarily decomposed material. In this connection, the formaldehyde still present (combined with hydrogen peroxide) must be taken into account, and the amount of acid oxidized can be calculated from the carbon loss.

We started with a mixture of 25 cc of a hydrogen peroxide solution (9.72 millimoles/cc) and 19.85 cc of a formaldehyde solution (7.74 millimoles/cc). After standing for 1 hour, the mixture was diluted to 70 cc and heated to 85 C in a flask provided with an air condenser. The results are given in Table 9.

TABLE 9

<u>Time,</u> <u>min</u>	<u>Acid</u> <u>mmol/cc</u>	<u>Peroxide,</u> <u>mmol/cc</u>
0	0.02	3.55
30	0.94	2.93
45	1.19	2.70
50	1.24	2.61
60	1.36	2.42
70	1.39	2.32
85	1.42	2.06

The perborate activity of this product, after neutralization of the formic acid, with sodium hydroxide, was 84 per cent. The solution contained 2.00 millimoles of carbon (elemental analysis) per gram. Of this amount, we may deduct 1.35 millimoles that are contributed by the formic acid (sp g of liquid, 1.05). Therefore 0.65 millimoles of carbon are combined as formaldehyde. This value corresponds to a value for β of 0.65/1.96 or 0.33.

The perborate activity interpolated from these results is 77 per

cent; the experimentally determined value was 84 per cent. This deviation is due to the presence of sodium formate; the solubility of sodium perborate in the reaction medium was lowered, and more precipitated. The starting material had a volume of 70 cc (sp g, 1.05). It contained 244 millimoles of hydrogen peroxide and 154 millimoles of formaldehyde ($\beta = 0.63$); the carbon content was therefore 2.10 millimoles per gram. By elemental analysis, we found 2.00 millimoles of carbon per gram; therefore, 0.10 millimole of carbon dioxide (4.8 per cent) must have been evolved. The results of this preliminary decomposition are summarized below:

TABLE 10

Starting material:	100 mmol H ₂ O ₂	63 mmol CHOH
64.4% HCOOH yield:	40.6 " " *	40.6 " "
Difference:	59.4 " "	22.4 " "
4.8% CO ₂ yield:	6.0 " " **	3.0 " "
Difference	53.4 " "	19.4 " "

* According to reaction (1).

** According to reaction (2).

2622

Thus we see that, if we assume that the formation of formic acid proceeds according to reaction (1) alone and that reaction (4) does not occur, 53 per cent of the peroxide remains. Actually, $100 \times 4.11/7.09$ or 58 per cent remains.

If the formation of formic acid proceeded according to reaction (2) alone, the initial peroxide content of 40.6 millimoles would be 20.3 millimoles and 74 per cent of the peroxide would remain. This percentage is much less in agreement with the experimental value of 58 per cent. Actually, both reactions (1) and (2) probably occur, (1) being predominant.

From the results in Table 10, it is apparent that a selective decomposition of the organic peroxides occurs, but not to such an extent that pure hydrogen peroxide remains.

#3. The Influence of Potassium Chloride on the Preliminary Decomposition

In orientational experiments, it was found that potassium chloride had considerable influence on the nature of the decomposition. No decrease in acid content occurred.

In an attempt to direct the preliminary decomposition in such a way that reactions (3) and (4) would not occur, we investigated further the influence of potassium chloride.

To 70 cc of a solution containing formaldehyde and hydrogen peroxide in a mol ratio of 0.63, was added 25 grams of potassium chloride. When the mixture was heated at 85 C, all the salt dissolved.

The concentrations of active oxygen and acid were determined as a function of time (Table 11).

TABLE 11

<u>Time,</u> <u>min</u>	<u>Acid,</u> <u>mmol/cc</u>	<u>Peroxide,</u> <u>mmol/cc</u>
0	0.04	3.09
15	1.31	..
60	1.50	1.10
75	1.52	0.74
90	1.51	0.61
120	1.53	0.43
150	1.54	0.31

2623

Results of the preliminary decomposition of the same solution in the absence of potassium chloride are given in Table 12.

TABLE 12

<u>Time,</u> <u>min</u>	<u>Acid,</u> <u>mmol/cc</u>	<u>Peroxide,</u> <u>mmol/cc</u>
0	0.02	3.55
30	0.94	2.93
45	1.19	2.70
50	1.24	2.61
60	1.56	2.42
70	1.39	2.32
85	1.42	2.06

(See also Fig. 4)

These results show that potassium chloride accelerates the decomposition. In addition, the formic acid formed is not further oxidized. Reaction (3) is thus repressed, and this repression is an advantage. The yield of pure hydrogen peroxide should then be 40 to 70 per cent. Unfortunately, however, reaction (4) plays a predominant role and thus nullifies the advantage gained by repressing reaction (3).

In order to study the influence of potassium chloride on a solution obtained by the oxidation of propane, the decomposition of active oxygen and the formation of formic acid in such a solution was investigated in the presence and in the absence of potassium chloride.

The solution studied was prepared by the reaction of 90 parts of propane with 10 parts of oxygen at a contact time of 4.1 seconds and had a perborate activity of 45 per cent. We started with a dilute solution of these peroxides, to which was added, at first, potassium chloride in a concentration of 25 grams per 70 cc.

The results are given in Table 13 and in Fig. 5.

TABLE 13

2624

Time, min	Without KCl		With KCl	
	Acid, mmol/cc	Peroxide mmol/cc	Acid, mmol/cc	Peroxide, mmol/cc
0	0.07	3.48	0.07	3.24
30	0.42	3.26	0.68	2.46
60	-	-	1.00	1.77
90	0.90	2.82	1.20	1.51
120	1.08	2.59	1.27	0.82
150	1.31	2.27	1.29	0.57
210	1.33	1.67	1.23	0.21
270	1.28	1.23	1.27	0.09
330	1.21	0.95	1.25	0.03

In this case also, the addition of potassium chloride seemed to accelerate reaction (4). Nothing definite can be concluded from this experiment in regard to the suppression of reaction (3). The suppression is, however,

clearly shown in other experiments.

A perborate activity of 45 per cent corresponds to an aldehyde-hydrogen peroxide mol ratio of 0.87 (8). On this basis, we arrive at acid yields of 44 and 45 per cent, respectively.

The decomposition curves for propane peroxides in the presence and in the absence of potassium chloride have the same course as the curves obtained with a mixture of hydrogen peroxide and formaldehyde. Thus the earlier assumption (5) that propane peroxides consist of mixtures of, principally, formaldehyde and hydrogen peroxide appears justified.

Acid formation in true propane peroxides proceeds more slowly in both cases, and the acid yield is somewhat lower than in formaldehyde-hydrogen peroxide mixtures.

From the work described in this section, it is apparent that potassium chloride inhibits the further oxidation of the organic acid formed during the decomposition. The decomposition of hydrogen peroxide to water and oxygen, on the other hand, is accelerated. Thus, as a whole, the preliminary decomposition in the presence of potassium chloride is unsatisfactory.

#4. Influence of Temperature and of Active Oxygen Concentration of the Nature on the Preliminary Decomposition

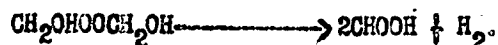
2625

In the preliminary decomposition of propane peroxides, we had always worked at an arbitrarily chosen temperature. We had wondered whether it might be possible to conduct the preliminary decomposition more favorably under somewhat modified conditions. By "more favorably" is meant with less active oxygen loss and with more nearly complete conversion of organic peroxides to acid.

In order to investigate this matter, peroxide decomposition and formic acid formation in the initial stage of the preliminary decomposition were determined at different temperatures. In one experiment, the concentration was also varied.

The results are given in Table 14 and in Fig. 6.

It appeared that, under all the conditions investigated, (temperature, 50 to 100 C; concentration, 1 to 6 millimoles of active oxygen per cc), the primary reaction was one in which, for each mole of acid formed, 1/2 mole of active oxygen disappeared. This reaction can be none other than:



After a time, the further reactions mentioned on frame 2620 set in. This happened when the ratio of acid formed to peroxide decomposed became zero.

TABLE 14

Time, min	Active O Present, mmol/cc	Acid Present, mmol/cc 95 C	Active O Decomposed, mmol/cc	Acid Formed, mmol/cc
0	5.82	0.04	-	-
4	5.88	0.29	0.14	0.25
8	5.57	0.78	0.45	0.74
10	4.79	1.45	1.03	1.44
17	4.11	1.82	1.71	1.78
31	3.22	1.97	2.60	1.93

2626

78 C				
Time, min	Active O Present, mmol/cc	Acid Present, mmol/cc	Active O Decomposed, mmol/cc	Acid Formed, mmol/cc
0	5.83	0.06	-	-
6	5.81	0.26	0.02	0.20
12	5.43	0.58	0.40	0.52
19	5.27	0.95	0.56	0.89
28	4.94	1.24	0.89	1.18
101	3.06	1.95	1.77	1.89

68 C				
Time, min	Active O Present, mmol/cc	Acid Present, mmol/cc	Active O Decomposed, mmol/cc	Acid Formed, mmol/cc
0	5.62	0.07	-	-
15	5.62	0.30	0.00	0.23
33	5.36	0.69	0.26	0.52
56	5.05	0.95	0.57	0.88
86	4.63	1.27	0.99	1.20

61 C				
Time, min	Active O Present, mmol/cc	Acid Present, mmol/cc	Active O Decomposed, mmol/cc	Acid Formed, mmol/cc
0	5.70	0.05	-	-
29	5.57	0.27	0.13	0.22

(Continued)

Table 14 (Continued)

Time, min	Active O Present, mmol/cc	Acid Present, mmol/cc	Active O Decomposed, mmol/cc	Acid Formed, mmol/cc
6l C				
70	5.36	0.64	0.34	0.59
120	5.01	1.01	0.69	0.96
184	4.54	1.36	1.16	1.31
256	4.09	1.61	1.61	1.56
3l C				
0	5.82	0.04	-	-
18	5.66	0.30	0.16	0.26
41	5.42	0.60	0.40	0.56
80 C; 5-fold dilution				
0	1.12	0.011	-	-
11	1.08	0.068	0.04	0.057
20	1.06	0.137	0.06	0.126
52	0.99	0.218	0.13	0.207

The conclusion from this work is that the operating conditions have no noticeable effect on the nature and the kinetic relations of the preliminary decomposition.

#5. Investigation of the Duration of the Preliminary Decomposition with Simultaneous Removal of Formic Acid

Removal of formic acid during the preliminary decomposition should be a desirable feature. One should be able to accomplish this removal in a column through which steam is passed (see Part 3, #3), provided that the residence time of the solution and the temperature in the column are so chosen that complete conversion of the organic peroxides occurs.

In order to investigate this possibility, several experiments were conducted. Since the formic acid would be directly removed by the steam passing upward in the column, the acid had to be removed regularly in our experiments in order to simulate the proposed conditions.

The simulation was accomplished by interrupting the process at predetermined intervals and charging fresh mixtures, in which the hydrogen peroxide concentration in formaldehyde was equal to that in the reaction mixture before interruption and which contained no formic acid.

In contrast to the process conducted in a column, a predetermined amount of hydrogen peroxide was used to oxidize the acid formed.

In order to increase the similarity between the experiments and the phenomena occurring in a column, a correction was applied to the hydrogen peroxide content. The correction was calculated from the difference between the total number of millimoles of formaldehyde and formic acid and the total number of millimoles of formaldehyde originally present.

The acid concentration was determined by titration with sodium hydroxide. The hydrogen peroxide was determined by the method of Kingzett (8) (sample allowed to stand with acidified potassium iodide solution in the dark for at least half an hour). The formaldehyde was determined by the method of Blank and Finkenbeiner (13).

The first experiment was conducted at 70 C. The results are given in Table 15 and in Fig. 7. For the sake of brevity, only the concentrations (mmol/cc) at the moment of interruption in each experiment are given. The starting material was a mixture of hydrogen peroxide in formaldehyde ($\phi \approx$ ca. 0.60).

TABLE 15

2628

Time, min	HCHO, mmol/cc	HCOOH, mmol/cc	HCOOH, mmol/cc corr.	H ₂ O ₂ , mmol/cc	H ₂ O ₂ , mmol/cc, corr.	ϕ ,* corr.
0	3.55	0.05	0.05	5.73	5.73	0.62
45	2.57	1.04	1.04	5.10	5.10	0.50
90	1.85	1.65	1.75	4.47	4.57	0.40
0	1.89	0.04	0.04	4.65	4.65	0.41
45	1.64	0.26	0.29	4.56	4.59	0.36
90	1.44	0.46	0.49	4.41	4.44	0.32
135	1.25	0.63	0.68	4.24	4.29	0.29

* $\phi = \text{HCHO}/\text{H}_2\text{O}_2$, corr.

(Continued)

Table 15 (Continued)

Time, min	HCHO, mmol/cc	HCOOH, mmol/cc	HCOOH, mmol/cc, corr.	H ₂ O ₂ , mmol/cc	H ₂ O ₂ , mmol/cc, corr.	ϕ
0	1.21	0.03	0.03	4.26	4.26	0.28
45	1.19	0.13	0.13	4.25	4.25	0.28
90	1.06	0.23	0.26	4.14	4.17	0.26
135	0.97	0.31	0.35	4.03	4.07	0.24
180	0.89	0.37	0.43	3.90	3.96	0.22

It thus appears that the decomposition at this temperature requires a very long time, so that the practical applicability is rather low.

Subsequent experiments were conducted at 90 C (see Table 16).

TABLE 16

Time, min	HCHO, mmol/cc	HCOOH, mmol/cc	HCOOH, mmol/cc, corr.	H ₂ O ₂ , mmol/cc	H ₂ O ₂ , mmol/cc, corr.	ϕ
0	5.53	0.05	0.05	5.80	5.80	0.61
10	1.83	1.71	1.75	4.65	4.69	0.39
0	1.88	0.04	0.04	4.90	4.90	0.38
10	1.61	0.34	0.34	4.59	4.59	0.35
20	1.20	0.70	0.75	4.27	4.32	0.28
0	1.16	0.03	0.03	4.34	4.34	0.27
10	1.03	0.13	0.16	4.21	4.24	0.24
20	0.94	0.25	0.25	3.96	3.96	0.24
30	0.79	0.33	0.40	3.86	3.88	0.20
40	0.71	0.46	0.48	3.73	3.75	0.19
60	0.63	0.52	0.56	3.47	3.51	0.18
90	0.50	0.55	0.69	3.10	3.24	0.15
120	0.45	0.52	0.74	2.86	3.08	0.15

(See also Fig. 8)

Although in this case, the decomposition was much more rapid, several hours were required for more or less complete decomposition. The value of ϕ decreased to 0.15. It seems that further decrease of ϕ would be very slow.

It is noteworthy that the periodic removal of formic acid decreases the velocity of the decomposition.

Since 90 C would be considered rather a high temperature (above 90 C, hydrogen peroxide decomposes rapidly into water and oxygen), it is believed that the residence time in the column required for complete decomposition is too great to make the process commercially suitable.

#6. Preliminary Decomposition in Alkaline Medium

As shown in the foregoing work, the preliminary decomposition could not be conducted, by the method used, in such a way as to effect complete decomposition of the organic peroxides.

We attempted to find means for improving the process. A means was found which comprised conducting the decomposition in the presence of alkalis. In the dissertation of Chijsen (10), it was stated that, in the decomposition of mixtures of hydrogen peroxide and formaldehyde in the presence of alkalis, the formaldehyde is converted quantitatively to formic acid. The question was whether, in such a treatment of a solution having a perborate activity of 60 per cent, a satisfactory amount of hydrogen peroxide would remain undecomposed: i.e. whether the decomposition would be selective.

The first experiment was conducted at 15 C. The starting material was a mixture of hydrogen peroxide and formaldehyde in which the formaldehyde-hydrogen peroxide mol ratio was 0.60 and in which the active oxygen concentration was 1.8 millimoles per cc. The active oxygen concentration was deliberately made low because, at higher concentrations, the decomposition would be expected to be too rapid. To several portions of the solution, 20.0 cc of 0.938 normal potassium hydroxide per 15 cc was added. After a certain time interval (different for the different portions), the decomposition was stopped by complete neutralization with 25.0 cc of 0.834 normal sulfuric acid. The active oxygen and the formic acid in each portion were then determined.

The results are given in Table 17 and in Fig. 9.

TABLE 17

2630

Time	Peroxide,		Formic Acid	
	mmol total	%	mmol total	%
0	26.6	100	-	-
10 min	23.5	88	5.2	31
1 hr	19.3	73	10.7	67

(Continued)

Table 17 (Continued)

Time	Peroxide.		Formic Acid	
	mmol total	%	mmol total	%
2 hr, 10 min	16.8	82	12.8	81
4 hr	15.8	69	13.5	85
22 hr	10.6	40	16.0	100

From these results, we see that, after 22 hours, 40 per cent of the hydrogen peroxide remains, whereas all the formaldehyde is converted to formic acid.

In order to determine whether raising the temperature would increase the amount of hydrogen peroxide remaining, an "alkali decomposition" was conducted at 42 C. The results were identical except for the fact that the reaction velocity was considerably greater.

Although the preliminary decomposition in the presence of alkali gives lower hydrogen peroxide yields than the other methods, it has the advantage of yielding a product completely free from organic peroxides.

An additional matter that occupied our attention was the recovery of the hydrogen peroxide from the alkaline solution. Direct vacuum distillation was not to be considered, because hydrogen peroxide is unstable in alkaline solutions. Therefore we added an excess of sulfuric acid and vacuum distilled the resulting acid solution. Considerable loss (about 70 per cent) of active oxygen occurred, probably as a result of the reaction of the sulfuric acid with the potassium formate to produce formic acid, which increased the pH too greatly.

The only possibility of operating without high loss is to add sufficient sulfuric acid to convert all the potassium formate to formic acid. The disadvantage of such a method is that, during distillation, some formic acid distills with the hydrogen peroxide and must subsequently be removed.

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In addition, this method of operation requires rather large amounts of potassium hydroxide and sulfuric acid. We calculated that about 1.0 kg of potassium hydroxide and 1.7 kg of 96 per cent sulfuric acid per kg of 30 per cent hydrogen peroxide are required.

For these reasons, it is believed that preliminary decomposition in the presence of alkali is not very attractive commercially.

LABORATORY

N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ

AMSTERDAM, August 31, 1942

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FIG. 1

APPARATUS FOR SELECTIVE WASHING OF COMBUSTION
GASES FROM PROPANE PEROXIDE PREPARATION

Invoer propaan & O ₂	-	Inlet for propane & oxygen.
Thermoelement	-	Thermocouple
Gasmeter	-	Gas meter
Koelwater	-	Cooling water

FIG. 2

DECOMPOSITION OF PROPANE PEROXIDES AT 85°C.

concentratie, mmol/cc	-	concentration, mmol/cc
tijd in minuten	-	time, min
zuur	-	acid
peroxyde	-	peroxide

FIG. 3

STEAM DISTILLATION APPARATUS FOR PREPARATION
OF HYDROGEN PEROXIDE

midden invoer	-	intermediate inlet
condensvat	-	condensate trap
verwarming	-	heater
stoom snelheidsmeter	-	steam flowmeter
buisje om lucht door te borrelen	-	tube for bubbling air through water bath

koeler	-	condenser
vacuumaftap inrichting	-	vacuum connection
verwarmings wikkeling	-	heating element
contact thermometer	-	thermometer
verwarmings element	-	heater

FIG. 4

2636

DECOMPOSITION OF A FORMALDEHYDE-HYDROGEN
PEROXIDE MIXTURE ($\rho = 0.63$) IN THE PRESENCE
AND IN THE ABSENCE OF POTASSIUM CHLORIDE AT 85 C

Peroxydeontleding	-	Peroxide decomposition
mmol/cc	-	mmol/cc
Zonder KCl	-	Without KCl
Met KCl	-	With KCl
Tijd in min	-	Time, min
Zuurforming	-	Acid formation

FIG. 5

2637

DECOMPOSITION OF PROPANE PEROXIDES (pba = 45%)
IN THE PRESENCE AND IN THE ABSENCE OF POTASSIUM
CHLORIDE AT 85 C.

Peroxydeontleding	-	Peroxide decomposition
mmol/cc	-	mmol/cc
Zonder KCl	-	Without KCl
Met KCl	-	With KCl
Tijd in min	-	Time, min
Zuurforming	-	Acid formation

FIG. 6

2658

DECREASE OF PEROXIDE CONCENTRATION WITH TIME
AT DIFFERENT TEMPERATURES

mmol peroxyde/cc	--	mmol peroxide/cc
minuten	--	minutes

DECOMPOSED PEROXIDE AS A FUNCTION OF ACID FORMED

(verdund)	--	(diluted)
oorsprong	--	tangent at origin
mmol zuur/cc	--	mmol acid/cc

FIG. 7

2659

PRELIMINARY DECOMPOSITION AT 70 C WITH PERIODIC
REMOVAL OF FORMIC ACID

mmol/cc	--	mmol/cc
gecorr.	--	corrected
tijd in uren	--	time, hr

FIG. 8

PRELIMINARY DECOMPOSITION AT 90 C WITH PERIODIC
REMOVAL OF FORMIC ACID

tijd in min	--	time, min
gecorr.	--	corrected
mmol/cc	--	mmol/cc
tijd in uren	--	time, hr

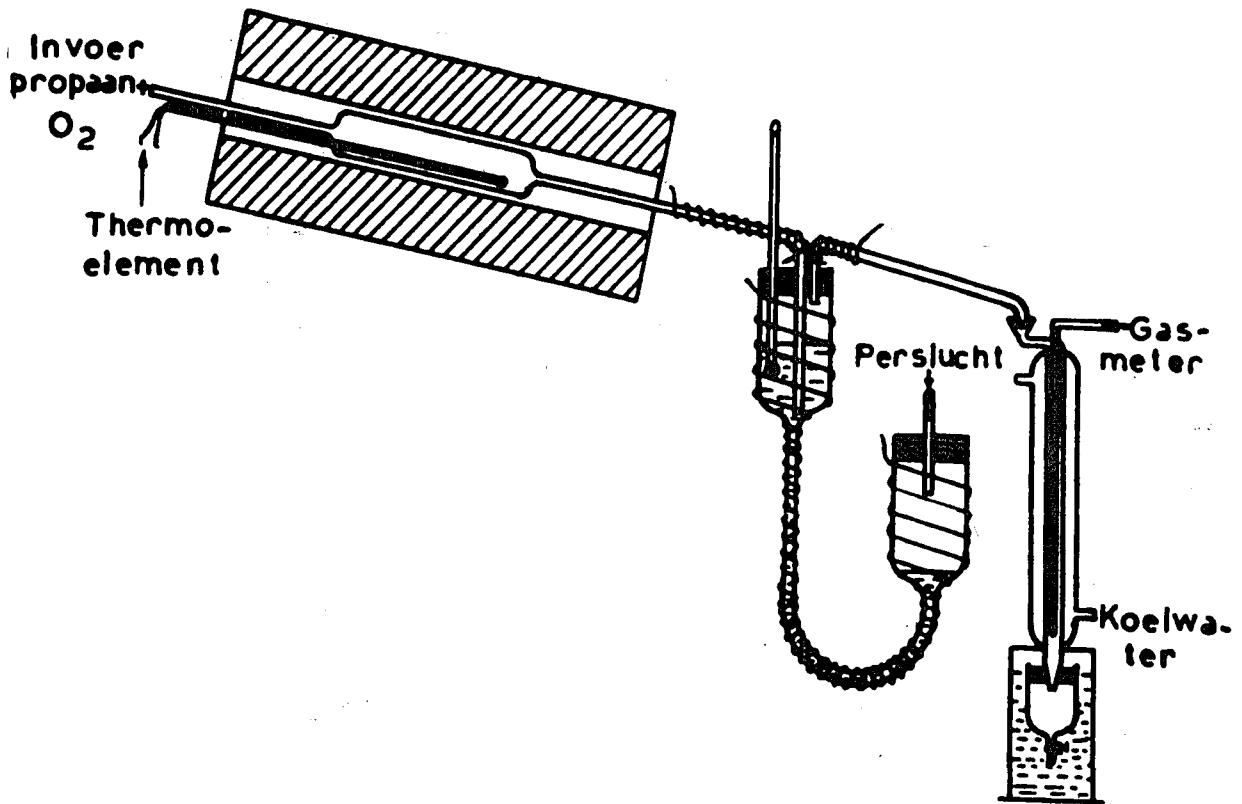
FIG. 9

2840

PRELIMINARY DECOMPOSITION AT 15 C IN THE PRESENCE
OF POTASSIUM HYDROXIDE

mmol totaal	--	total mmol
zuur	-	acid
peroxyde	-	peroxide
tijd in uren	-	time, hr

APPARATUUR VOOR DE SELECTIEVE WASSCHING
VAN DE VERBRANDINGS-GASSEN VAN
DE PROPANPEROXYDENBEREIDING

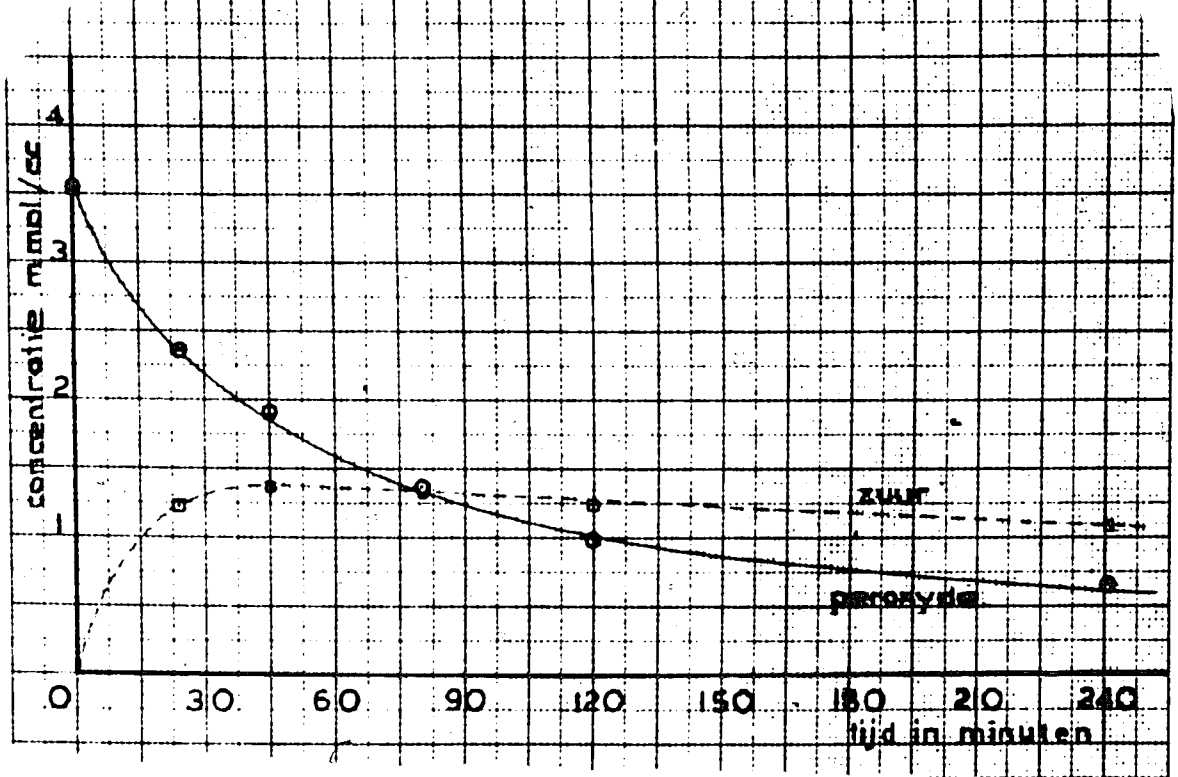


002634

fig. 2

DE ONTLEDING VAN PROPANPEROXYDEN

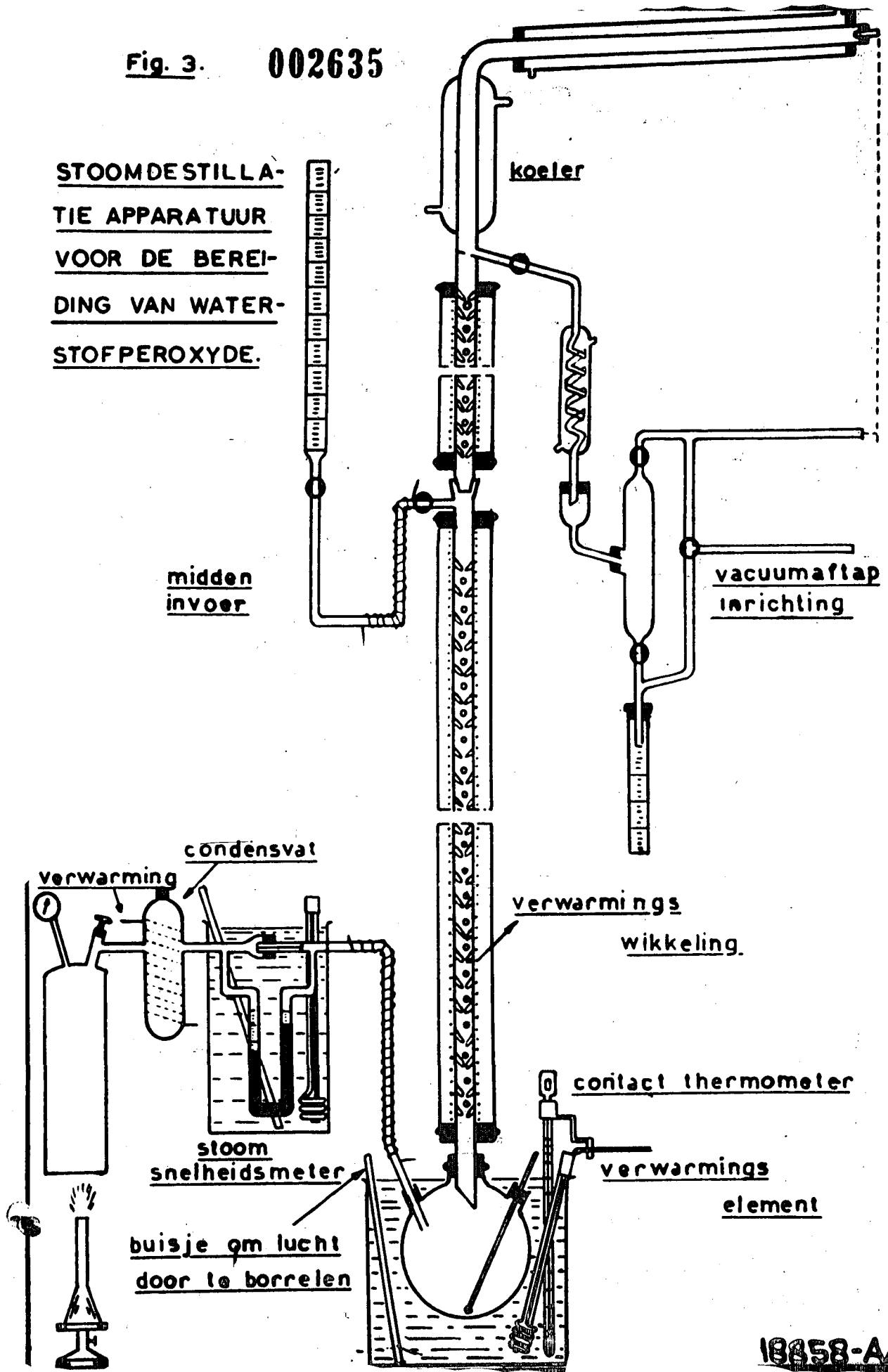
BIJ 85°C.



5647-54

Fig. 3. 002635

STOOMDESTILLA-
TIE APPARATUUR
VOOR DE BEREI-
DING VAN WATER-
STOF PEROXYDE.



18858-A4

De ontleding van een kromzilver/AgO₂-
mengsel (p = 0,53) met en zonder KCl bij 50°C

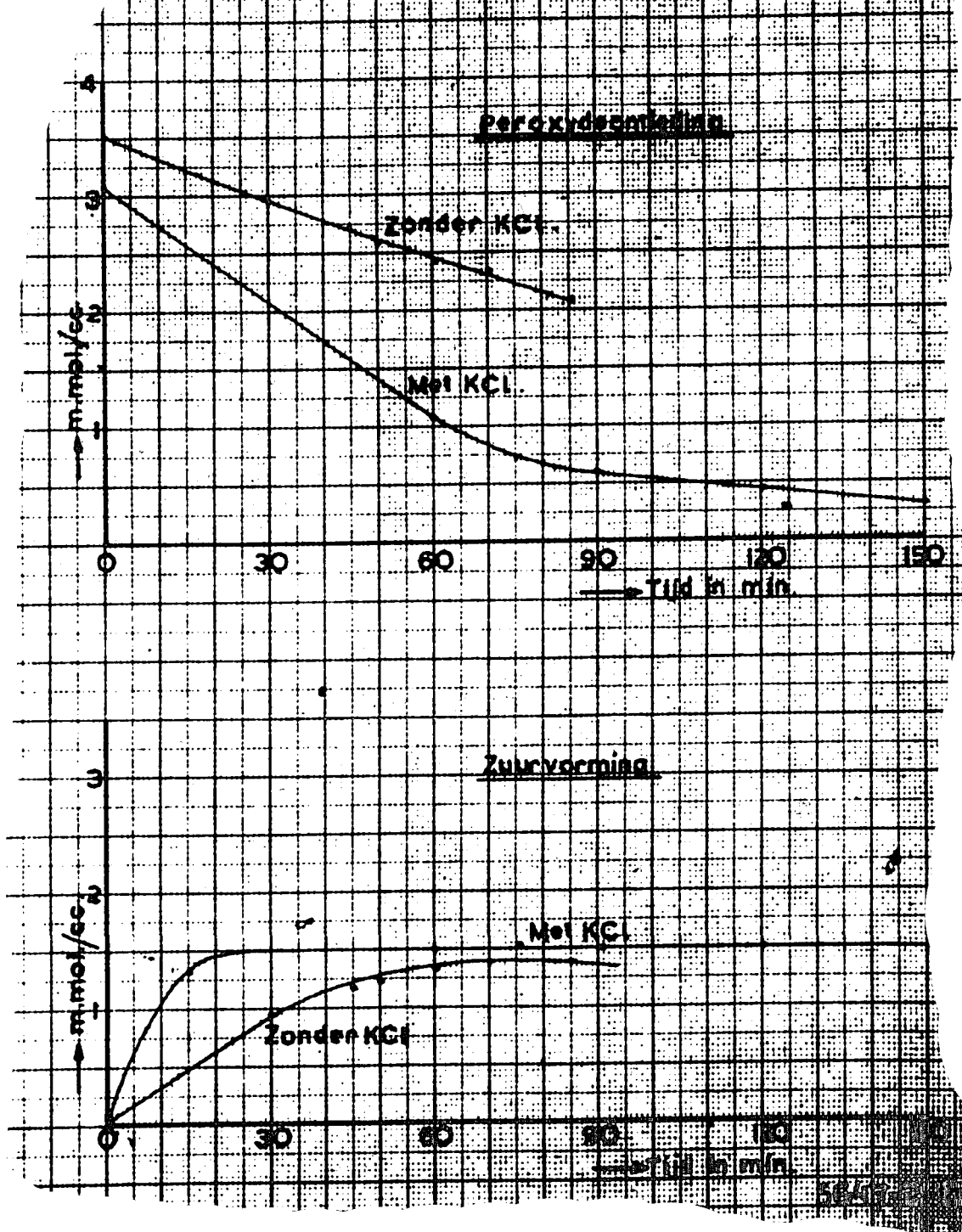
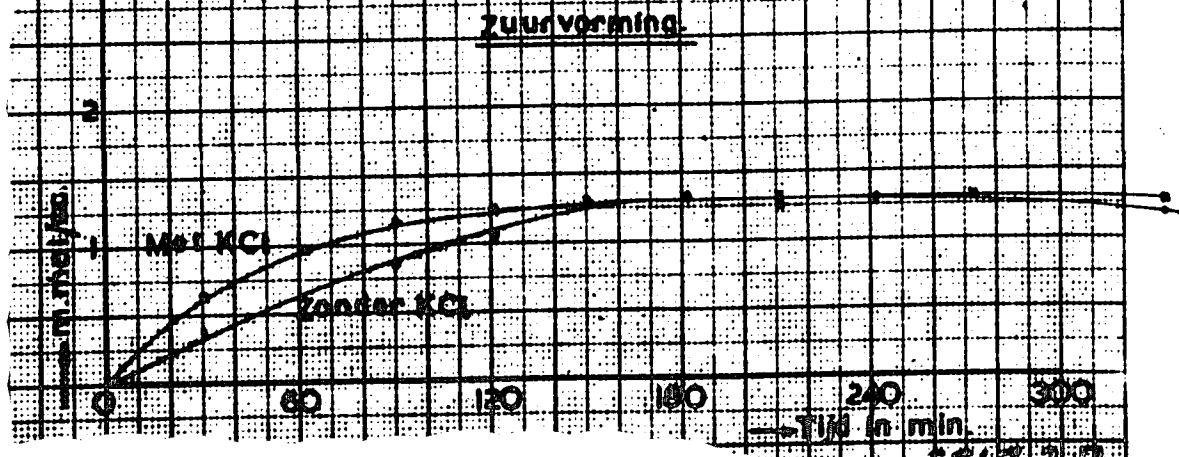
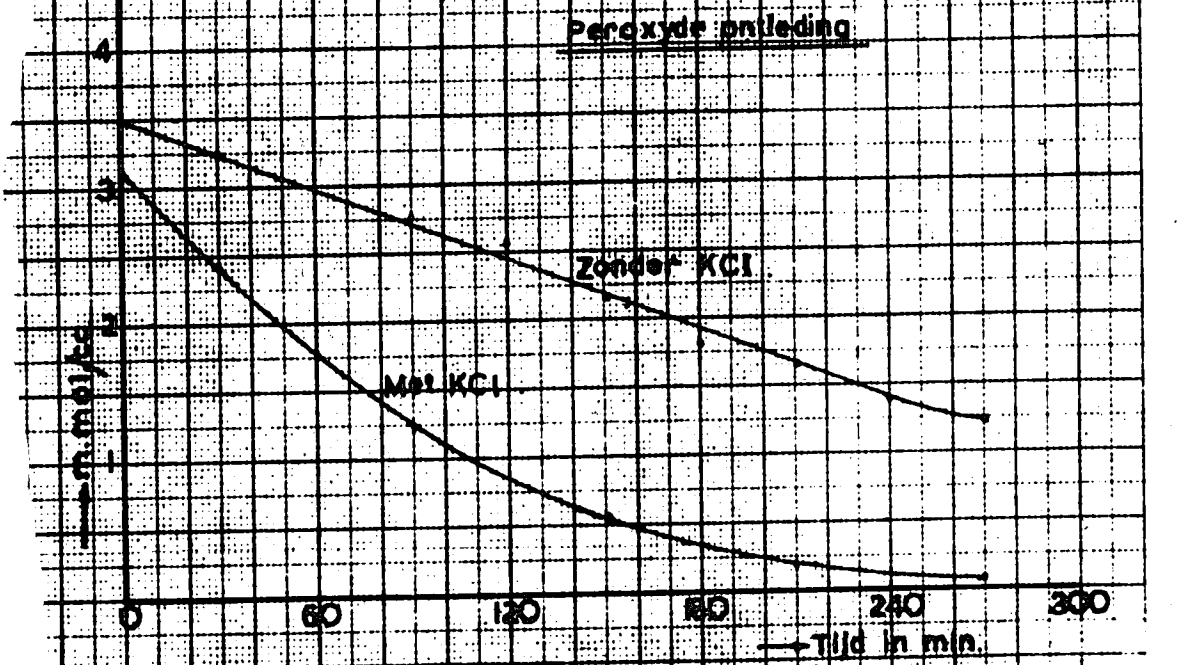


Fig 5

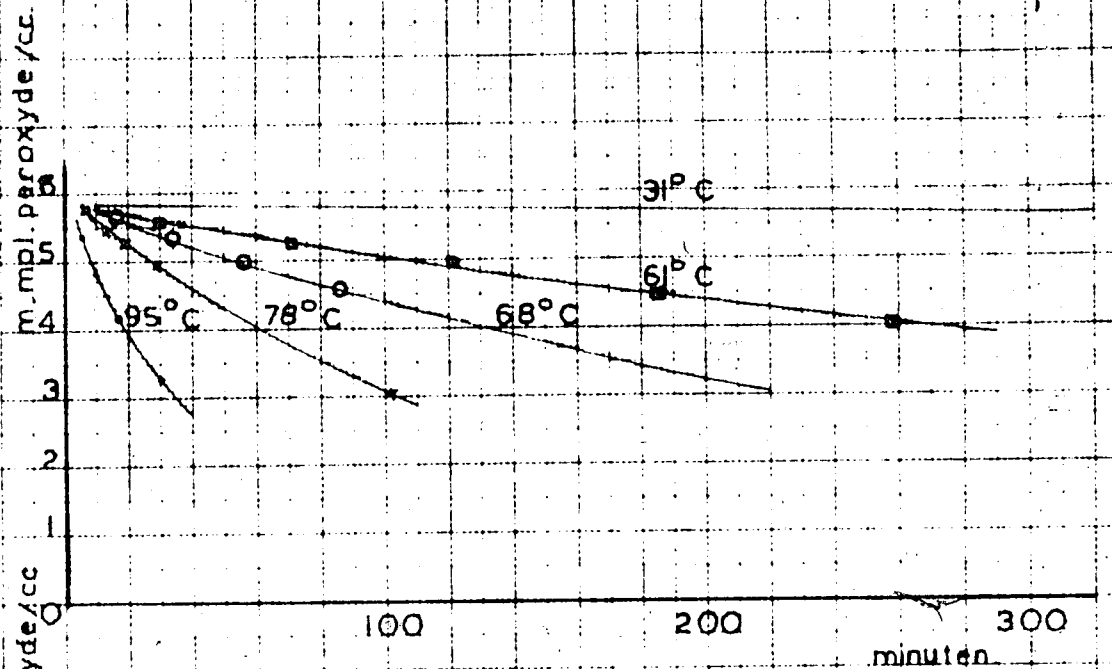
De ontleding van propaanperoxyden (pha = 45%)
 met en zonder KCl, bij 85°C



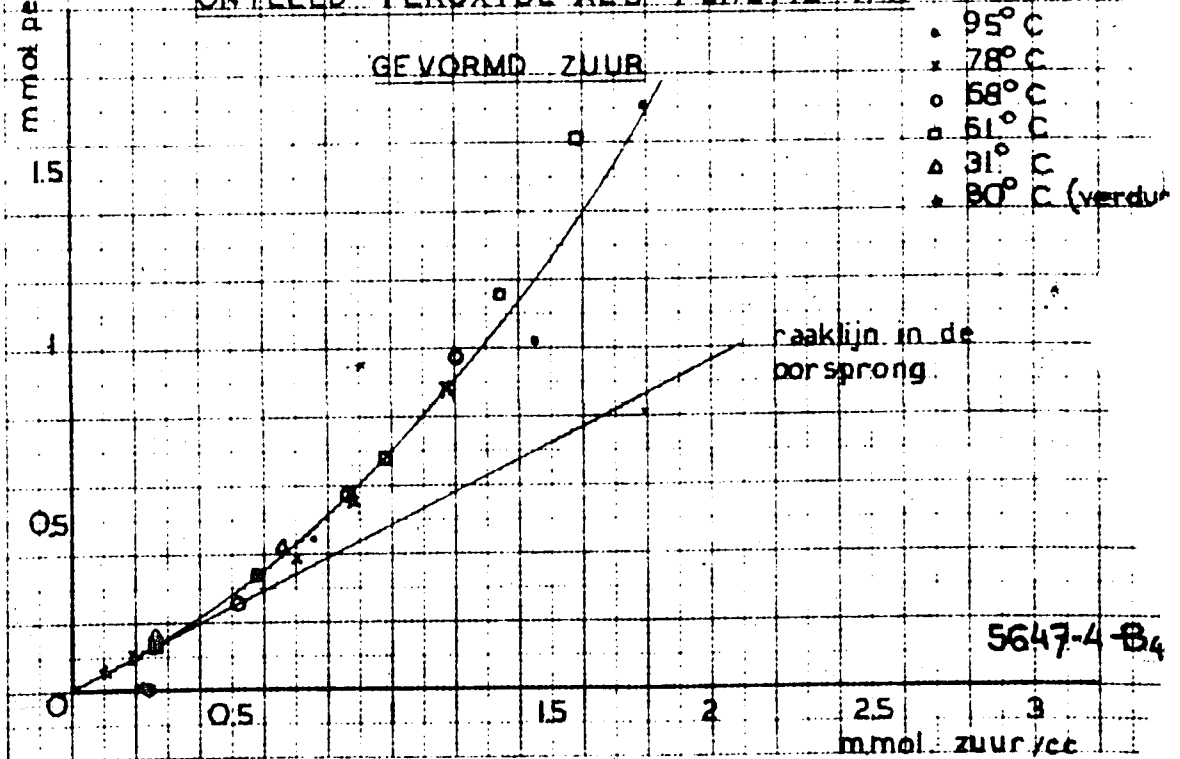
5547-2-3

Fig. 6

AFNAME VAN DE PEROXYDECONCENTRATIE MET
DEN TIJD BIJ VERSCHILLENDE TEMPERATUREN.



ONTLEED PEROXYDE ALS FUNCTIE VAN
GEVORMD ZUUR



5647-4-84

Fig. 7.

DE VOORONTLEDING BIJ 70°C MET TUSSEN.
TIJDSCHE VERWIJDERING VAN HET MIERENZUUR

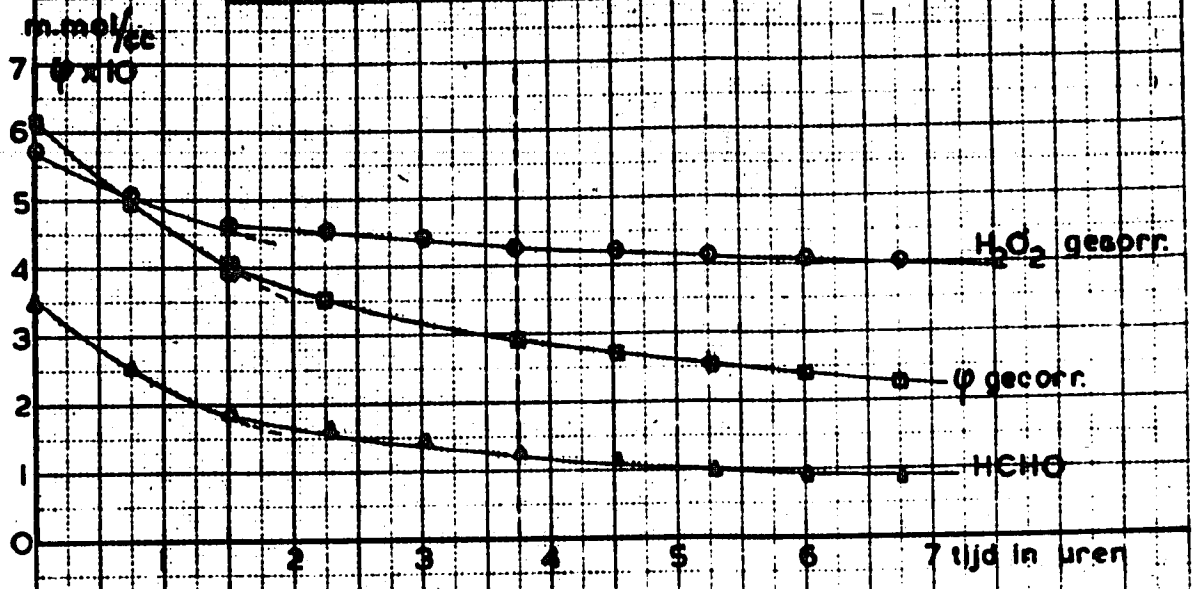


Fig. 8.

DE VOORONTLEDING BIJ 90°C MET TUSSEN.
TIJDSCHE VERWIJDERING VAN HET MIERENZUUR

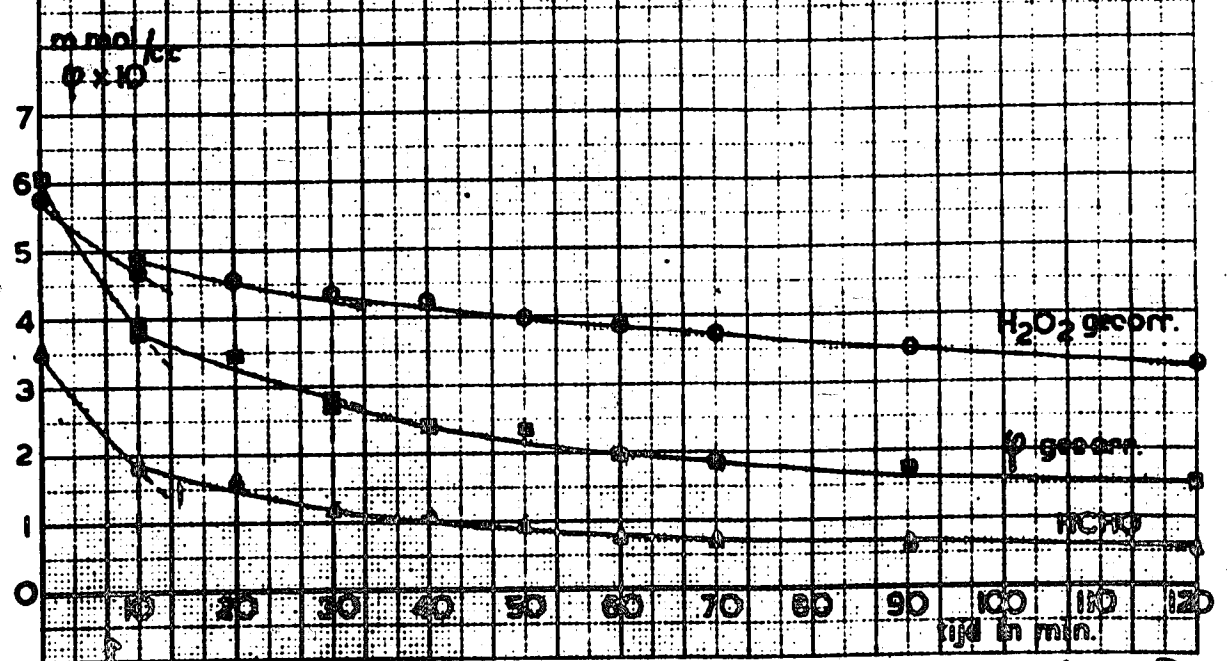
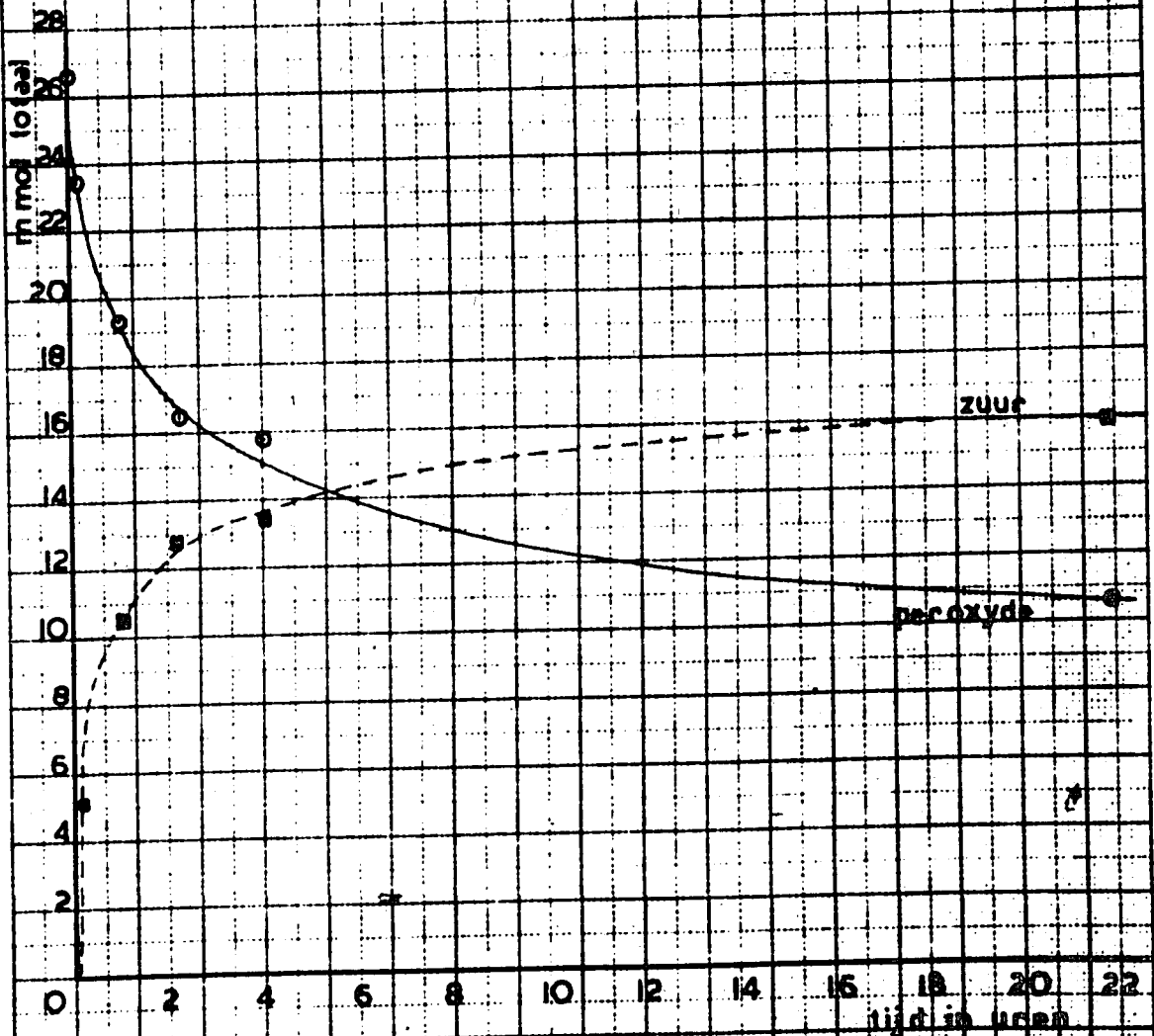


Fig. 9

VOORONTLEDING BIJ 15°C ONDER INVLOED
VAN KOH.



3547.6-1