Report 9269

INVESTIGATION OF THE STRUCTURE OF UNSATURATED HYDROCARBONS IN CRACKED DISTILLATES BY THE PERACETIC ACID METHOD

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Translation

SUMMARY

Investigations by Boeseken and Stuurman have established that 2369
the rate of oxidation of unsaturated hydrocarbons with peracetic acid depends strongly on the hydrocarbon structure. The 1-olefins, which are the most valuable polymerization components in cracked distillates, are characterized by an especially small reactivity toward peracetic acid.

The present investigation advances the work done by the above-named investigators by the determination of oxidation-rate constants for a number of pure olefins. The experimental work and the preparation of peracetic acid are described in this report.

The data obtained for pure olefins were used in an investigation of the mixtures of unsaturated compounds present in cracked distillates. The course of each oxidation was depicted by a so-called oxidation curve; the possibility of numerical characterization of this curve was ascertained.

Oxidation curves were obtained for a number of different types of cracked distillates (Balik Papan, Dubbs, U.O.P., Rhenania) and for fractions of these distillates. The results led to the following conclusions:

1. The structure of the olefins in cracked distillates is indicated by the oxidation curve obtained by the peracetic acid method. Various cracked distillates can be especially well compared with respect to the content of 1-olefins. 2370

2. Comparison of various Rhenania cracked distillates indicates that the oxidation curve does not provide an unobjectionable criterion of the quality of the distillate as a raw material for polymerization.

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I. Introduction

Vapor-phase cracking of paraffin produces so-called cracked distillates, which serve as raw material for preparation of synthetic lubricating oil by polymerization. These cracked distillates consist mostly of unsaturated hydrocarbons boiling between 0 C. and 500 C., corresponding to molecular weights between about 50 and about 250. With respect to the structure of the unsaturated hydrocarbons, it is known that by far the best are the unbranched 1-olefins and that the next best are the unbranched 2- and 3-olefins.

In addition, depending upon the cracking feed and the cracking conditions, there are present some olefins and diolefins of branched and cyclic structures; also, some aromatic hydrocarbons, chiefly benzene derivatives.

Investigations by Sullivan (1), Koch and Hilberath (2) and Zorn (3) have established that 1-olefins, without branching at the double bond, give much better yield and quality of lubricating oil on polymerization than do the unbranched 2- and 3-olefins, whereas cyclic olefins and olefins with branching near the double bond are generally inferior feeds for polymerization. In consequence, the great differences in suitability of cracked distillates from various sources, for polymerization to lubricating oil, are to be attributed to differences in the content of unsaturated hydrocarbons of good, less good, and poor structures. However, such differences do not account for every variation

(1) F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland, Ind. Eng. Chem., 23, 604 (1931).
(2) H. Koch and F. Hilberath, Brennstoffchem., 23, 67 (1942).
(3) Zorn, Schriften der deutschen Akademie für Luftfahrtforschung (Publications of the German Academy for Aeronautical Research), 9, 71(1939).

in polymerization, for it is possible that small amounts of catalyst poisons may be of decisive influence. Nevertheless, the primary condition for obtaining good results is a high content of normal 1-olefins; consequently, it is important to have available a method for determining this group of compounds. So far as is known, such a method has not been described in the literature. 2375

Such a method should meet the following requirements:

1. The results should make possible a reliable estimate of the content of normal 1-olefins in comparison with other types of unsaturated compounds.

2. The method should be simple and rapid.

Comparison of the chemical and physical properties of normal 1-olefins with those of other monoolefins indicated that the possibility of finding a good basis for such a method was not great. The presence of diolefins and of aromatic hydrocarbons was unfavorable, and the large range of molecular weights was a big obstacle. If narrow fractions were to be obtained to overcome these difficulties, the method would be too cumbersome in practice.

From the analytical viewpoint, the most favorable possibility appeared in the differences found by Boeseken and Stuurman (4,5,6) in the rate of oxidation of various olefins by peracetic acid. The values compiled in Table I illustrate their findings for the rate of oxidation of pure olefins.

Table I

Hydrocarbon	Type	Oxidation rate constant (25.8 C), $k \times 10^5$
1-Pentene	C=C-	4.3
1-Hexene	"	4.9
1-Heptene	"	5.5
2-Butene	-C=C-	93
2-Pentene	"	94
2-Hexene	"	99
3-Hexene	"	129
2-Methylpropene	C=C<	92
2-Methyl-2-butene	-C=C<	980

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These data demonstrate that the normal 1-olefins have a much smaller rate of oxidation than the normal 2- and 3-olefins. Also, they show that increase in the number of alkyl groups at the double

(4) J. Stuurman, Diss. Delft (1936).
(5) J. Boeseken and J. Stuurman, Proc. Acad. Sci. Amsterdam, 39, 2 (1936).
(6) J. Boeseken and J. Stuurman, Rec. Trav. Chim., 56, 1054 (1937).

bond is accompanied by a marked increase in the rate of oxidation. Finally, they indicate that the rate for each particular olefin type is only slightly affected by the molecular weight. These relatively favorable indications suggested an investigation of the possibility of determining the type of unsaturated compounds in cracked distillates by measuring the rate of oxidation.

II. Oxidation Experiments with Pure Olefins

1. The purpose of making experiments with pure olefins was twofold: to develop the proper oxidation technique and to increase the available data for the behavior of particular types of unsaturated hydrocarbons in oxidation with peracetic acid.

2. The investigated hydrocarbons were synthesized by Dr. G. Verberg, partly for addition to the laboratory's collection of hydrocarbons and partly for the oxidation experiments. They were purified before use by careful fractionation in a column of about 20 theoretical plates. The 2- and 3-olefins were mixtures of cis- and trans-isomers. From the results obtained by Stuurman, it was already known that stereoisomerism had apparently no great influence on the rate of oxidation. The investigation of distillate fractions containing various stereoisomers did not seem to require separation of the cis- and trans-isomers.

3. Preparation of the peracetic acid was by substantially the method given by Stuurman: To a mixture of hydrogen peroxide having a concentration of about 45 per cent and 5 weight per cent of concentrated sulfuric acid in a round-bottomed flask was added enough acetic anhydride in small portions to react completely with the water and the hydrogen peroxide, according to the following equations:

$$H_2O + (CH_3CO)_2O \longrightarrow 2CH_3COOH$$

$$H_2O_2 + (CH_3CO)_2O \longrightarrow CH_3COOH + CH_3COOOH$$

After each addition of acetic anhydride, the reaction mixture was thoroughly agitated. The temperature was continually observed; it was not permitted to exceed 30 C., by regulating the rate of addition of acetic anhydride. Cooling the flask with ice water made possible a satisfactorily rapid rate of addition.

After all of the acetic anhydride had been added, the reaction mixture was allowed to come to room temperature and was tested for the presence of acetyl peroxide (Caution! Danger of explosion!), by adding 1 ml. of the reaction mixture to a glass-stoppered Erlenmeyer flask containing a solution of potassium iodide acidified with sulfuric acid. The following reactions occurred:

$$CH_3COOOH + 2HI \xrightarrow{\text{rapid}} I_2 + CH_3COOH + H_2O$$

$$(CH_3COO)_2 + 2HI \xrightarrow{\text{slow}} I_2 + 2CH_3COOH$$

Accordingly, titration with 0.1 N thiosulfate in presence of starch determined the peracetic acid, and further titration of the "after-bluing" determined the acetyl peroxide. The amount of thiosulfate required to titrate the afterbluing formed in an hour must not be more than 8 per cent of the amount required in the first titration. By the preparative method used, a lower afterbluing was always obtained.

The peracetic acid was then vacuum-distilled in an all-glass apparatus. The pressure was so regulated that the distillation temperature was 25-35 C. Higher pressures were attended by danger of explosion, whereas much lower pressures made condensation of the distillate difficult. In order to retain the acetyl peroxide in the residue, the distillation should not be carried too far, but should be discontinued as soon as the volume has decreased to a fifth of the original volume, and the residue should not be worked up further.

The distillate thus obtained contains about 20 per cent peracetic acid and decomposes only very slowly.

4. The oxidation experiments were made also according to the method 2376
developed by Stuurman. All experiments were carried out at 25 C in glacial acetic acid as a dilution medium. The glacial acetic acid could contain only little water, to avoid decreasing the solubility of hydrocarbons in the reaction mixture. Furthermore, a blank experiment had to be made to ascertain the absence of oxidizable impurities. By fractional distillation of chemically pure glacial acetic acid, a product was always obtained that satisfied these requirements.

The concentrations of the peracetic acid and the olefins were made as nearly equal as possible and were always about 0.05 mole per liter.

The determination of rate constants for the oxidation was as follows:

A weighed amount of olefin was added to about 475 ml. of glacial acetic acid in a 500-ml. volumetric flask, which was placed in a thermostat. After the contents had come to temperature, 10 ml. of peracetic acid solution was added, and the flask was rapidly filled to the mark with glacial acetic acid. The mixture was quickly made homogeneous by shaking, and the first 50-ml. sample for titration was withdrawn. As the initial moment for the reaction was taken the moment when the pipette containing the peracetic acid solution being added became half emptied.

At predetermined times additional 50-ml. samples were withdrawn and were added to Erlenmeyer flasks containing potassium iodide solution acidified with glacial acetic acid. The liberated iodine was titrated with thiosulfate in the presence of added starch solution. As the reaction time for the sample was taken the moment when the pipette became half emptied.

The initial concentration of the peracetic acid was not generally determined separately, but was found by extrapolation. The amounts of thio-

sulfate required for the first three titrations were plotted against the time; however, for fast reactions, it was better to plot the reciprocals of the amounts of thiosulfate used. Almost straight lines, which could be readily extrapolated to t = 0, were obtained.

The oxidation rate constants were calculated by the general equation for a bimolecular reaction: 2377'

$$Kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

in which t = time in minutes
a = initial concentration of peracetic acid in moles per liter
b = " " " olefin " " " ".

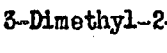
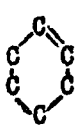
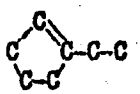
Inasmuch as almost equivalent concentrations of the reactants were used, it was advantageous to use the following approximate equation:

$$Kt = \frac{1}{c-x} - \frac{1}{c}$$

in which $c = (a \pm b)/2$.

5. The results of the oxidation experiments are summarized in Table II. They demonstrate the very strong influence of the structure of the olefin on the rate of oxidation with peracetic acid. The rate constants found for 1-heptene, 1,5-hexadiene and cyclohexene agree very well with the values given by Stuurman. The value for 3-heptene is lower than that found by Stuurman.

Table II

Hydrocarbon	Structural Formula	Oxidation rate constant (25 C.), K x 10^3
1-Heptene	C=C-C-C-C-C-C	5.6
2-Heptene	C-C=C-C-C-C-C	92.3
3-Heptene	C-C-C=C-C-C-C	94.3
1-Octadecene	C=C-$(C)_{15}$-C	[illegible]
1,5-Hexadiene	C=C-C-C-C=C	8
2,3-Dimethyl-1-butene		85.9
2,3-Dimethyl-2-butene		10500
Cyclohexene		128.6
Ethylcyclo-1-pentene		3000

These data showed that the normal 1-olefins are characterized 2378
by an exceedingly small reactivity toward peracetic acid, whereas the normal olefins with more centrally located double bonds are considerably more rapidly oxidized, with no great difference being apparent between 2- and 3-olefins. Introduction of alkyl groups near the double bond increases the oxidation rate markedly. The oxidation rate constant for 1-octadecene could not be determined with high accuracy because of the low solubility of this olefin in glacial acetic acid; nevertheless, the result was in complete harmony with the supposition that the molecular weight has little influence on the reactivity. From the value obtained for 1,5-hexadiene, the oxidation of this type of diolefin proceeds as for the normal 1-olefins. The rate constants for cyclohexene and for cyclopentene (Stuurman: $K \times 10^5 = 195$) show that cycloolefins, even in the absence of side chains, are rapidly oxidized.

The so-called oxidation curves are very helpful in indicating the course of the oxidation for different types of structures. These curves show the concentration of peracetic acid in the reaction mixture, expressed in ml. of 0.1 N thiosulfate used for 50 ml. of reaction mixture, as a function of time; see Figure 1. These curves serve also for comparison with the results of the next-described experiments, with cracked distillates of various kinds.

III. Oxidation Experiments with Cracked Distillates

1. General remarks follow on peracetic acid oxidation of olefin mixtures, such as those present in cracked distillates.

The oxidation curves for pure olefins of a given initial concentration of the reactants form a family of curves that pass through the same point only at $t = 0$. With the help of the above-given equation for a bimolecular reaction, an oxidation curve can be readily constructed for any value of the rate constant. For a mixture of compounds having the same 2379
oxidation-rate constants, the oxidation curve approximates those for the individual compounds. For a mixture of compounds having different oxidation-rate constants, the course of the reaction is less clear, inasmuch as the highly reactive components are completely converted in a short time, and the course of the reaction in its later stages is determined by the compounds with relatively small oxidation-rate constants; consequently, the oxidation curve diverges from the curves for the pure compounds, and its shape depends on the relative amounts and the K-values of the unsaturated compounds present.

Among the unsaturated compounds forming the major part of a cracked gasoline there is a great variety of structure types, which means a great spread in the reactivity toward peracetic acid. For estimating the kind and the amount of structure types from the oxidation curve, it is fortunate that the differences in structure types lead to considerable stepwise changes in the oxidation rate constant and that the especially interesting normal 1-olefins form a distinct group having extremely low reactivity.

Inasmuch as differences in polymerization behavior may be traced to differences in kind and amount of the structure types present, especially the content of normal 1-olefins, these might be correlated with the form of

the oxidation curve. The possibility of characterizing the shape of the oxidation curve by numbers will be discussed later in section 5. Preliminarily may be considered the relationship of the shape of the oxidation curve to the properties of the cracked gasoline.

2. Determination of oxidation curves for cracked gasolines was under the conditions used in the oxidation experiments with pure hydrocarbons, in order to have a good basis for comparing results. That is, the oxidations were carried out in glacial acetic acid at 25 C. In order to simulate having almost equal concentrations of olefin and peracetic acid (about 0.05 mole per liter), the amount of cracked gasoline, which contained saturated hydrocarbons, aromatic hydrocarbons, diolefins, etc., as well as monoolefins, was so selected that the content of olefinic double bonds was equivalent to the 2380
peracetic acid. The content of olefinic double bonds was determined by the McIlhiney bromine-number method. It was realized that the desired goal was only approximated, inasmuch as the McIlhiney method has several sources of error, especially the fact that the double bonds of conjugated diolefins do not react quantitatively with bromine. It would have been ideal to utilize the van Westen hydrogen-number method (7), but this method requires a difficult and time-consuming technique. Inasmuch as it was likely that small amounts of sulfur and oxygen compounds present in the cracked gasolines reacted with peracetic acid and that the titration of peracid in the reaction mixture was likewise attended by an error owing to the rather strong afterbluing, the McIlhiney method appeared appropriate. For ordinary cracked gasolines, the errors introduced by the use of this method and by the presence of oxidizable nonhydrocarbon compounds were not expected to be so large as to disturb the general course of the oxidation.

3. Comparison of oxidation curves for several different types of cracked gasoline was made, using the 90-100 C. fractions obtained with a column of 20 theoretical plates from the following cracked gasolines:

a. Balik Papan cracked distillate. Inasmuch as cracked distillates of this type are characterized by a high content of normal 1-olefins, the 90-100 C. fraction should be chiefly 1-heptene.

b. Dubbs cracked distillate. Considerable amounts of 2- and 3-olefins could be expected, and also some cycloolefins; however, because the nature of the raw material cracked was not known, nothing about the latter could be predicted.

c. U.O.P. catalytically cracked distillate. Inasmuch as the cracking catalyst has a strong isomerizing activity, a considerable amount of branched 2- and 3-olefins would be expected.

The oxidation curves presented in Figure 1 indicate the influence 2381
of the structure of the unsaturated compound on the shape of the curve. Comparison with the curves of Figure 2 indicates that Balik Papan cracked distillate approximates a pure 1-olefin, although it doubtless contains also

(7) H. A. van Westen, Diss. Delft (1931).

compounds of higher reactivity. Dubbs cracked distillate contains large amounts of reactive olefins. The rapid decline at the beginning of the curve is to be attributed to the presence of normal 2- or 3-olefins or cycloolefins with side chains. After about 5 hours, the rate of oxidation becomes far less than that for normal 2- or 3-olefins, indicating definitely that this cracked distillate contains also a considerable amount of normal 1-olefin. The catalytically cracked distillate, as was expected, is much more rapidly oxidized than is the Dubbs gasoline.

4. Oxidation experiments with Rhenania cracked distillates. First were obtained oxidation curves for some fractions from Rhenania cracked distillate V 1118, which were isolated with a column of 22 theoretical plates. The distillation curves for gasolines prepared by vapor-phase cracking of paraffin always had more or less distinct plateaus because of the relative abundance of normal olefins (especially the 1-olefins). In the transitional regions between these plateaus, olefins with side chains or with cyclic structure appeared predominant. In consequence, an attempt was made during the fractionation to separate the plateau fractions from the transitional-region fractions, in the expectation that the former would differ from the latter in a much smaller rate of oxidation with peracetic acid. Comparison of the fractionation curve (Figure 3) with the oxidation curve (Figure 4) shows that this expectation was fulfilled. The initial very rapid reaction rate for Fractions 3 and 5 shows the presence of highly reactive components in the cracked distillate. Thus, from the standpoint of polymerization, the undesirable components had been concentrated in the transitional-region fractions.

Comparative experiments were also made with Rhenania cracked 2382 distillates V 1188, V 1189, V 1190, and V 1191. According to Prof. Zerbe's data, V 1190 had shown very unsatisfactory polymerization properties; the other cracked distillates had given good polymerization results. The oxidation curves of Figure 5 yielded no explanation of the divergent behavior of V 1190. The oxidation curve for this material falls practically on that for the good cracked distillate V 1189, and its differences from the curves for the other cracked distillates cannot be considered important. (It should be noted that the scale for the vertical axis is twice as large as for the earlier figures.)

Inasmuch as the Rhenania products did not have identical contents of volatile components nor identical end points, the oxidations were repeated for the 75-150 C. fractions obtained by fractionation of the cracked distillates in a column of 12 theoretical plates.

The oxidation curves for these fractions, in Figure 6, show a somewhat larger spread than those for the total cracked distillates. Although V 1190 again showed the highest reactivity, V 1189 had the smallest oxidation rate.

From the oxidation experiments it can be concluded that cracked

distillate V 1190 has a somewhat higher content of undesired components than the other Rhenania products. The difference in the oxidation curves, however, is so small as scarcely to account for the great difference in polymerization behavior. From the curves, it appears that the reactivity of a Rhenania product is always greater than that of a Balik Papan cracked distillate.

Further investigation, using fractions obtained with a column of 100 theoretical plates, revealed no differences with regard to either oxidation behavior or physical properties that indicated any considerable deviation in the composition of V 1190. It appears that the exceptional polymerization behavior of V 1190 should be attributed to the presence of a small amount of some catalyst poison. An oxidation curve obviously does not help in detecting such a poison, especially if it reacts rapidly with peracetic acid.

5. Characterization of the form of the oxidation curve of a cracked 2383
distillate, as by distinguishing numbers, would be very helpful in practical application of the peracetic acid method. For this purpose, it would be desirable to work as far as possible with a particular initial concentration of 0.05 mole per liter. For ascertaining the course of the curve, one could give the concentration of peracetic acid (expressed in ml. of 0.1 N thiosulfate required for 50 ml. of reaction mixture) at a number of agreed-upon times.

Theoretically, characterization according to the contents of a fixed number of structure types would be satisfactory. An attempt along this line might be realized in the following manner: Although the unsaturated compounds present in cracked distillates are imperfectly known as to type and as to reactivity with peracetic acid, they can be preliminarily classified into three classes:

a. Slightly reactive compounds, including 1-olefins with no branches near the double bond.

b. Moderately reactive compounds, including 2- and 3-olefins without branching at the double bond, 1-olefins with branching near the double bond, and cycloolefins without aliphatic side chains.

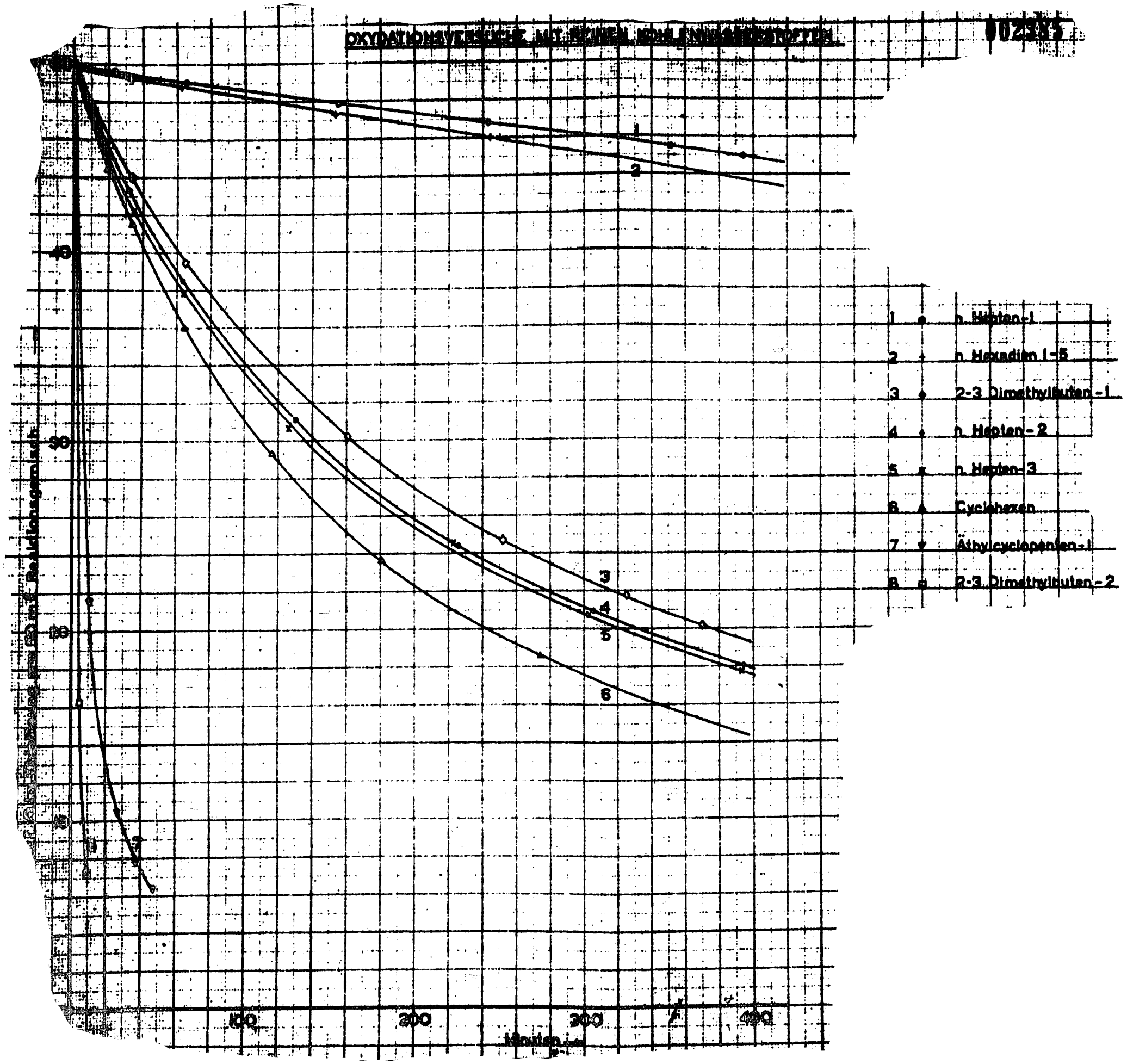
c. Strongly reactive compounds, including 2- and 3-olefins with branching at the double bond and cycloolefins with aliphatic side chains.

If for each of these classes a median value is taken for the oxidation rate constant, such as $K \times 10^5 = 5$, 100, and 2000, oxidation curves could be calculated for all possible mixtures of the three corresponding hypothetical components. By comparison of an actual oxidation curve with the series of calculated ones, a classification of the cracked distillate would be readily possible. However, the calculation of the theoretical curves would involve a system of simultaneous equations that could not be solved exactly, so that

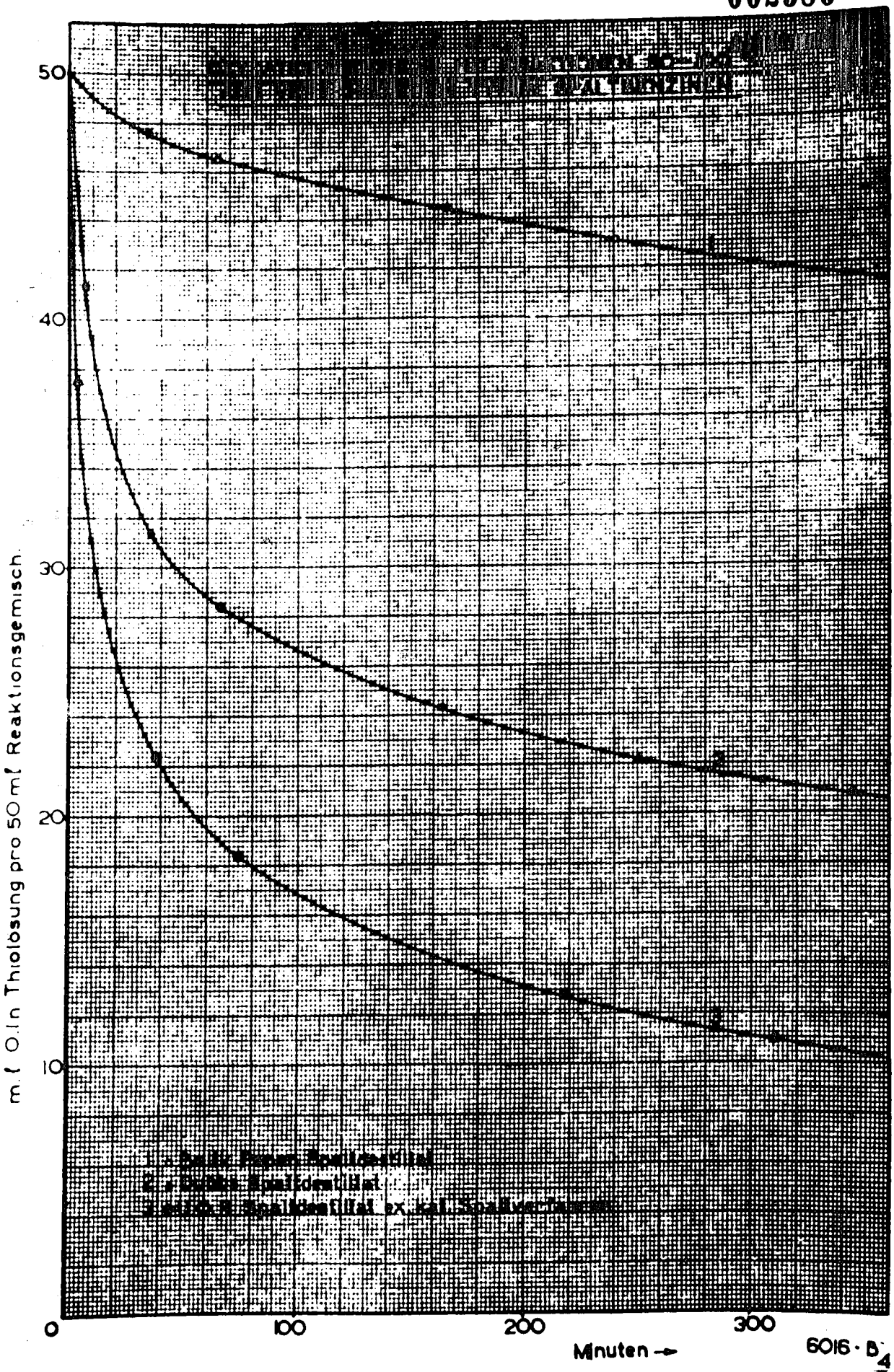
the working up of the data would require much time.

Of course, it would be possible to determine the series of curves through oxidation experiments with ternary mixtures of components having the necessary reactivities, but in view of the laboratory's unfavorable potassium iodide situation and of the fact that the oxidation curve for a Rhenania cracked distillate is no criterion of its polymerization quality, such a development is being left undone. 2384

OXYDATIONSVERSUCHE MIT REINEN KOHLENWASSERSTOFFEN



1 ● n. Hepten-1
2 ♦ n. Hexadien 1-5
3 ● 2-3 Dimethylbuten-1
4 ♦ n. Hepten-2
5 x n. Hepten-3
6 ▲ Cyclohexen
7 ▼ Äthylcyclopenten-1
8 ■ 2-3 Dimethylbuten-2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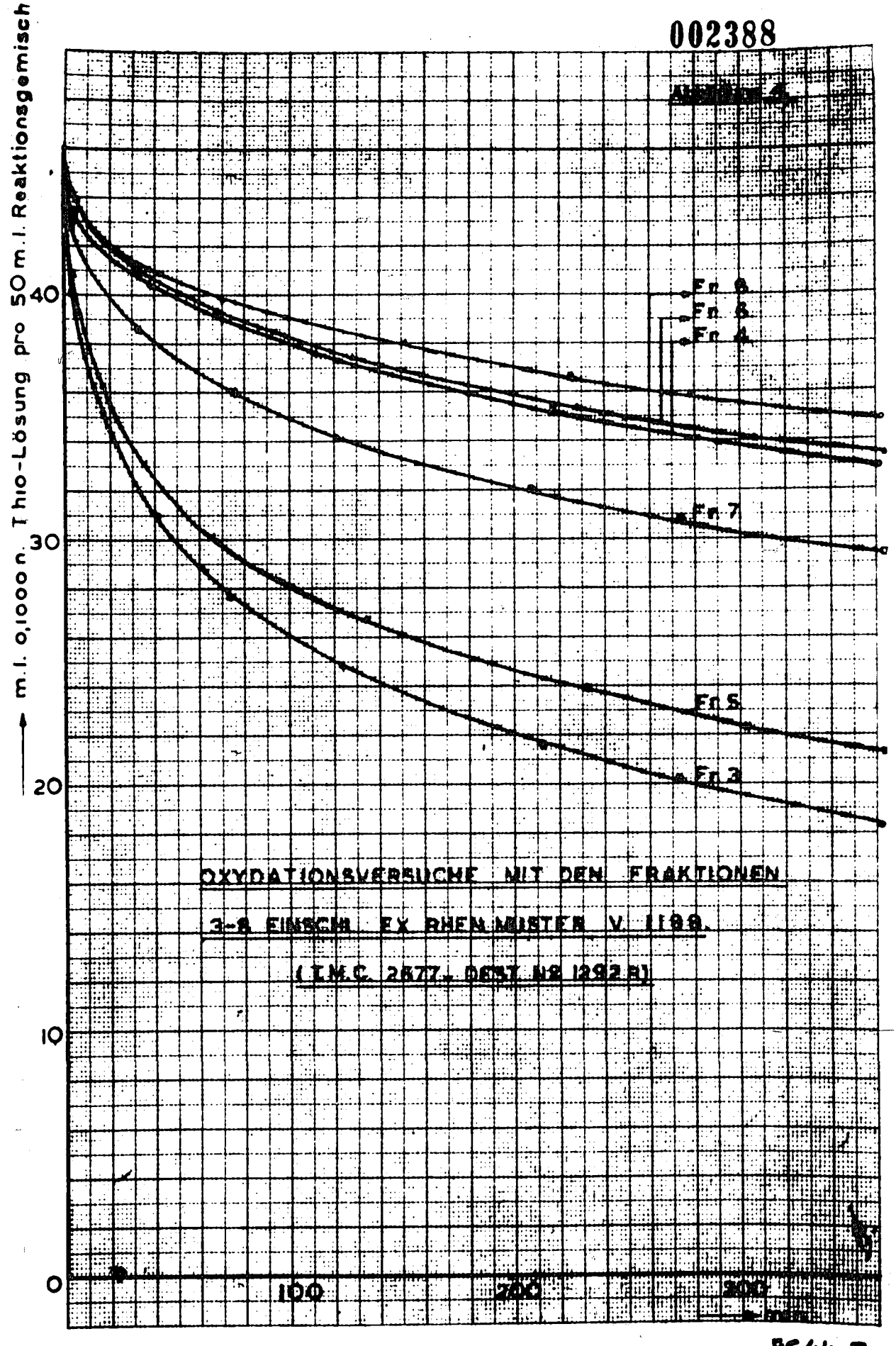

OXYDATIONSVERSUCHE MIT DEN FRAKTIONEN 3-8 EINSCHL. EX RHEN MUSTER V 1199.

(I.M.C. 2677. DEST NR 1292 A)

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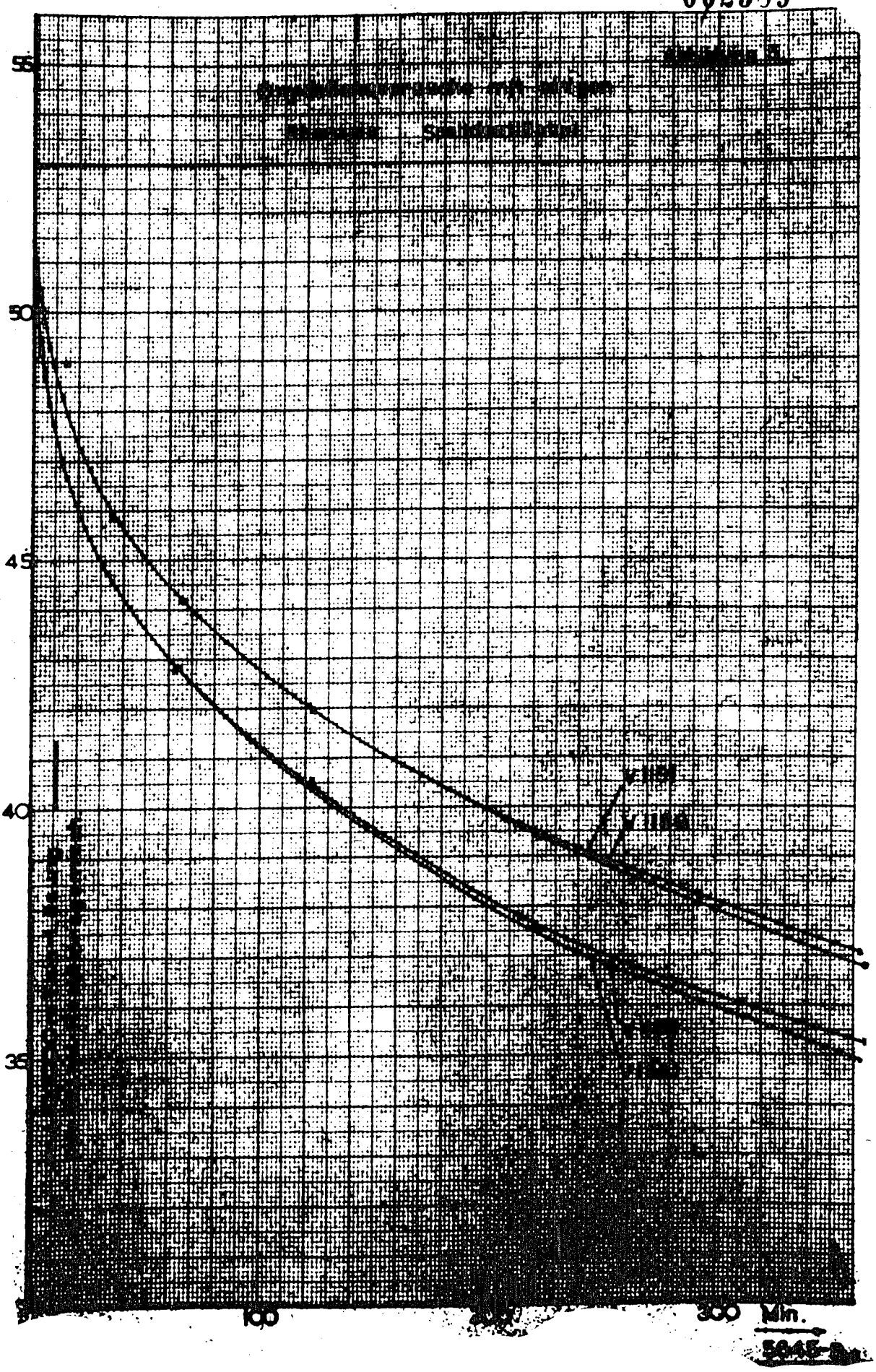

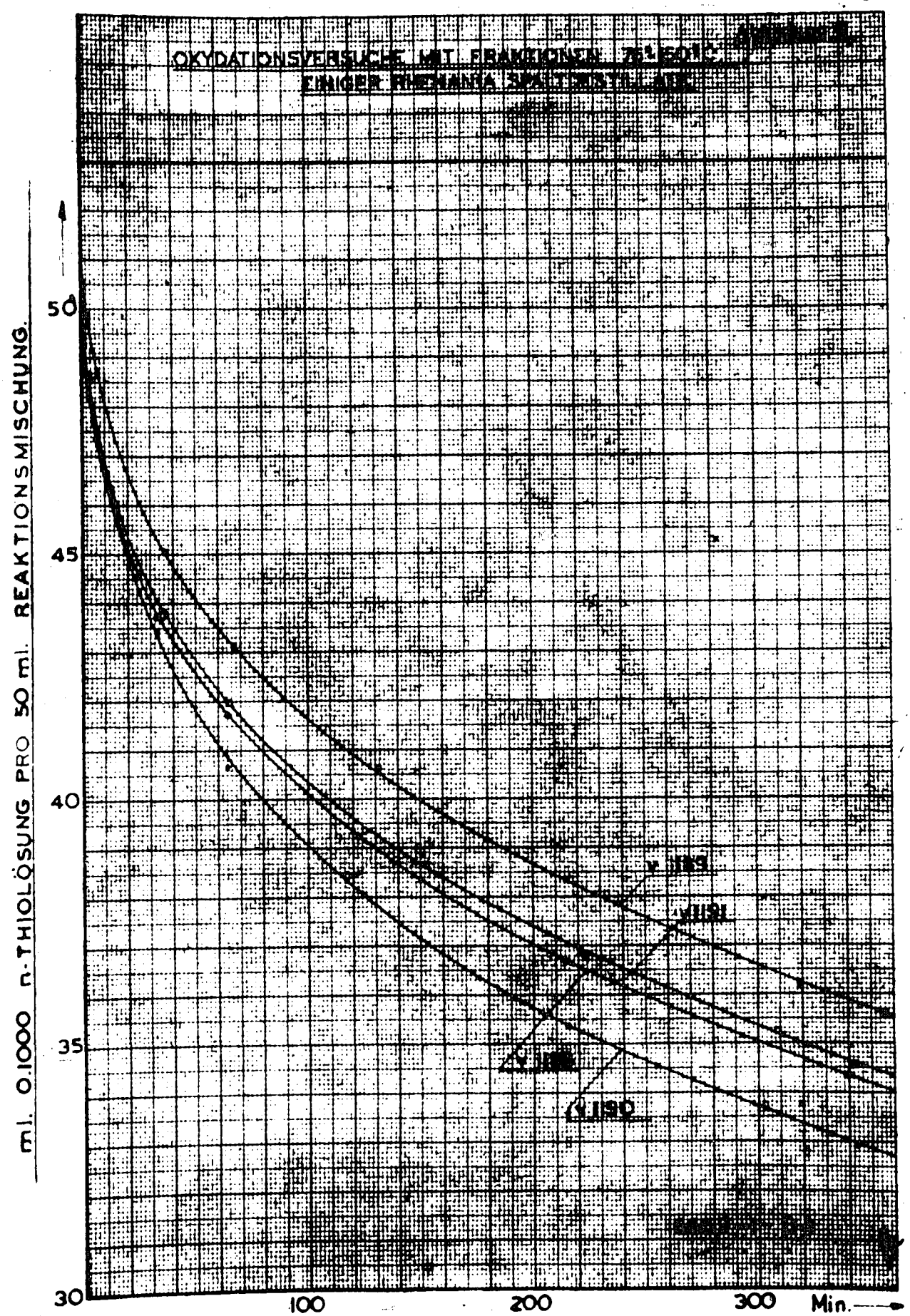
OXYDATIONSVERSUCHE MIT FRAKTIONEN 75%IGER
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ml. 0.1000 n-THIOLÖSUNG PRO 50 ml. REAKTIONSMISCHUNG.
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