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RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKEL--ETC(U)
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RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order I

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CONTRACT FULFILLMENT STATEMENT

This final report is submitted in partial fulfillment of Contract N7Onr-462, Task Order I.

SUMMARY

A. The objective of this contract is to prepare and characterize nitropolymers and to select those which may be useful in various military applications.

B. The most important results for the last quarterly period, 1 May 1957 to 31 July 1957, are summarized below.

1. A large number of potential polyurethane catalysts were screened for activity. Twelve new compounds were sufficiently active to warrant quantitative study.

a. Catalyst 119* is particularly interesting because of its high activity, which does not decrease in the presence of salts.

b. Catalysts 120 through 123 and 125 through 127 are of interest primarily because they are only moderately affected by salts.

c. Catalysts 124, 128, 129 and 130 were selected for quantitative study because they appear to have induction periods.

2. Catalysts 104 and 119 are effective in nitropolyurethane propellant formulations employing 5,5,5-trinitro-1,2-pentanediol (M), but thus far they have given only bubble-filled propellant castings in formulations containing 2,2-dinitro-1,3-propanediol (A).

3. Catalyst 114 was used successfully in both XIII-A-8X-0.6NPN-69AP and XIII-M-8X-0.6NPN-69AP propellant castings. The pot life in each case was greater than that of control castings employing ferric acetylacetonate.

4. The burning-rate catalyst, copper chromite, behaves as a polyurethane catalyst. Kinetic studies showed that a synergetic effect was obtained in the presence of ferric acetylacetonate.

5. Polyglycidyl nitrate (PGN-diol) exhibited a much lower rate of gas evolution after being washed with warm aqueous urea. The urea wash effected only slight improvement in the rate of gassing shown by PGNT-triol.

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*See List of catalysts in back of this report.

6. Binders and propellants stabilized by using urea-treated PGNT-triol and incorporating nitric acid scavengers showed little improvement, in gassing rate, over the unstabilized samples.

7. Appreciably lower yields than previously reported were obtained in the preparation of additional quantities of 5,5,5-trinitro-2-pentene for subsequent conversion to the corresponding epoxide. These results were assumed to be due to the use of low-quality 5,5,5-trinitro-2-pentanol.

8. Continued work on nitroepoxides, as a source of high-molecular-weight nitrodiols, was concerned with attempts to obtain these materials in high purity by means of chromatographic adsorption techniques in which neutral aluminum oxide was used. Despite promising data from prior work, this purification procedure, as presently developed, is not adaptable to all available nitroepoxides and the method lacks reproducibility, as is illustrated by the following results:

a. In the case of 5,5-dinitro-1,2-epoxyhexane, aluminum oxide failed to yield a pure material, although some improvement was effected.

b. With 5,5-dinitro-2,3-epoxyhexane, the procedure appeared to have the most promising possibilities; but reproducibility, particularly on scale-up, has been poor.

c. Glycidyl 4,4,4-trinitrobutyrate was not obtained in the pure state when an attempt was made to adapt the purification to larger scale, although this experiment was complicated by the use of a less pure starting material.

d. Some purification of 5,5,5-trinitro-2,3-epoxyhexane, using this technique, was previously reported. No further work has been done with this material.

9. The epoxide content of 5,5-dinitro-2,3-epoxyhexane was not affected by storage of this compound for 6 weeks at 0°C nor at ambient temperature for 1 week.

I. INTRODUCTION

During the preceding fiscal period, a final report (Aerojet Report No. 1162, 28 September 1956) was submitted to the Office of Naval Research which summarized the more important results obtained during research under Contract N7onr-462, Task Order I, at Aerojet-General Corporation during the period 15 August 1947 to 31 July 1956.

The report, of which this introduction is a part, represents a summary of that work performed under the same ONR contract during the period 1 August 1956 to 31 July 1957. Because previous reports (Quarterly Reports 1202, 1241, and 1281), covering the period 1 August 1956 to 30 April 1957, have included all experimental details of work performed during the indicated nine-month period, this particular report gives the experimental results of work performed from 1 May 1957 to 31 July 1957 only. However, all previous research is completely summarized and referenced in this report.

II. TECHNICAL PROGRESS: NITROPOLYMERS

A. CATALYST STUDIES

1. Introduction

Very early in the development of a nitropolyurethane propellant, the need for a catalyst became evident.[1] An efficient catalyst for the addition reaction of diisocyanates to diols was needed in order to allow short cure times at relatively low temperatures. Aside from the hazard, the high-temperature cure of a composite propellant is a serious obstacle to the preparation of a crack-free grain, especially with case-bonded propellants. The ideal catalyst would have low activity in the initial stages so that adequate mixing and casting time is available (pot life) and the majority of the heat evolved (exotherm) may be dissipated safely. The catalyst should have high activity during the final stages of polymerization. After complete cure, it is desirable that the catalyst lose its activity in order that rearrangement and degradation be at a minimum during storage. The catalyst must, of course, be compatible with the system and not catalyze side reactions that are detrimental to the desired properties of the final product.

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[1] Aerojet Report No. 457, 22 June 1950, p. 35 (Confidential);
Aerojet Report No. 482, 15 December 1950, p. 38 (Confidential).

Catalysis of the nitropolyurethane reaction has been studied previously under this contract.[1] The common acidic and basic catalysts were rejected because of one or more defects, including low activity, chain termination, or excessive decomposition of the nitro compounds. A number of neutral metallic complexes were studied; among them was ferric acetylacetonate. The discovery of this very active catalyst made practical the evaluation of the many potentially useful (but unreactive) monomers available for nitropolyurethane propellant formulations. Its use, however, involves the acceptance of a variety of disadvantages. Among these are poor pot life, deactivation by oxidizer (the "salt effect")[2], and deactivation by unknown, monomer-contained impurities. These disadvantages, together with the extremely high catalytic activity of ferric acetylacetonate, lead to a critical catalyst concentration which varies from batch to batch.

Consequently, the study of polyurethane catalysts was resumed. Emphasis was placed initially on the screening of readily available or readily prepared materials as potential catalysts. Materials which showed activity were examined in quantitative kinetic studies. Catalysts which showed promise were then tried in bulk polymerizations and, finally, in propellant castings. The prediction, from kinetic data, of the behavior in castings was only partially successful, possibly because of the necessity of using (in the kinetic studies) a different nitro-diol than those of current interest for propellant castings.[3] Another consideration is that during the curing of a casting, the all-important last few percentages of reaction take place in an extremely viscous medium, in contrast with the relatively dilute solution in the kinetic studies. Because of the lowered diffusion rate, some catalysts may lose their effectiveness because of failure to dissociate from an otherwise weak coordination with the already formed polymer. In other words, the catalyst may be

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[1] Aerojet Report No. 1162, 28 September 1956, p. 144 (Confidential).

[2] Aerojet Report No. 868, 17 September 1954, p. 39 (Confidential).

[3] Aerojet Report No. 1241, 15 March 1957, p. 4 (Confidential).

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"caged." Nonetheless, there was sufficient correlation to establish that the studies in solution were valuable. Catalyst evaluation (in castings only) would require many time- and material-consuming trials in order to bracket the catalyst concentration required.

In most polyurethane work, it is not essential to realize fully the properties of the ideal catalyst. One important objective of the recent program was the development of a catalyst whose activity remained essentially constant, instead of declining rapidly, during the polymerization. This objective was realized. In addition, the feasibility of delayed-action catalysis of nitropolyurethane formation was demonstrated.

In continuation of the policy to establish the relative reactivity of new monomer systems, the rate of polyurethane formation from the reaction of 3-nitraza-1,5-pentane diisocyanate (XIII) with polyglycidyl nitrate (PGN) was studied.

2. Discussion

a. Control Studies

The solution-polymerization of the XIII-J system (from 3-nitraza-1,5-pentane diisocyanate and 2-methyl-2-nitro-1,3-propanediol) was used in the catalysis studies. This system was chosen because of the availability of the monomers and because the system was compatible with a convenient method of isocyanate assay which could be used for following the rate of polymerization. In addition, these monomers were employed in most of the previous studies; hence, they offered a ready comparison of current with past work.

In order to compare various catalysts, it was assumed that the rate of polymerization was first-order with the catalyst. Thus, in the equation

$$DP = 1 + kC_o t \quad {}^{1}$$

where

$$k = k_c \text{ (catalyst)}$$

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[1] Aerojet Report No. 457, 22 June 1950, p. 32 (Confidential).

DP is the degree of polymerization, C_o is the initial monomer end-group concentration in moles per liter, t is the time in hours, k is the specific rate constant, k_c is the catalyst constant, and "(catalyst)" is the concentration of the catalyst in moles per liter. This equation appears to be valid once a critical catalyst concentration is reached; below this critical concentration, wide deviations may occur, presumably because of catalyst consumption. Each catalyst was tested for catalysis of the homopolymerization of XIII-diisocyanate, and in all cases studied, the rate was negligible ($k<10^{-3}$).

The uncatalyzed rate of XIII-J-nitropolyurethane formation is extremely low, with a k of approximately 10^{-3}. Data obtained on the catalytic effect of the urethane linkage showed that this effect was small enough to be disregarded in a catalyzed polymerization.[1] Although the same batch of J-diol was used throughout the studies, it was necessary to use several different batches of XIII-diisocyanate. Reproducibility of polymerization rate was excellent within a batch; however, as was previously recognized, there was considerable variation between batches.[2] From first-order dependence on catalyst concentration, the deviation between batches and the apparent deviation within a batch are adequately explained on the basis of an essentially instantaneous destruction of a fixed amount (dependent on batch) of catalyst.[3] The destruction is not quantitative; some residual activity remains. The critical catalyst level varied from approximately 1×10^{-6} to 3×10^{-5} mole of catalyst per equivalent of isocyanate in the batches of diisocyanate examined.

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[1] Aerojet Report No. 1241, 15 March 1957, p. 5 (Confidential).

[2] Ibid., p. 4.

[3] Ibid.; Aerojet Report No. 1281, 14 June, p. 4 (Confidential); Table 1 and Figure 1 of this report (No. 1318).

Acetylacetone had no effect on an otherwise uncatalyzed polymerization, but its presence markedly decreased the catalytic activity of ferric acetylacetonate. Other β-dicarbonyl compounds showed similar action.[1] It is recommended that this effect be studied in propellant castings, since this technique may offer a means of easily regulating the activity of ferric acetylacetonate.

b. The "Salt Effect" with Ferric Acetylacetonate

It has long been recognized that a higher concentration of ferric acetylacetonate catalyst is needed for the cure of a casting than for the binder resin alone. This additional "threshold" requirement ("salt effect") was qualitatively studied in some detail in castings.[2]

It was desired to evaluate the "salt effect" of new catalysts by means of more informative kinetic studies made in solution. In order to assess the feasibility of this method of evaluation, solid sodium chloride was suspended, by stirring, in a solution-polymerization catalyzed by ferric acetylacetonate.[3] The loss of catalyst activity was readily followed. A similar study with ammonium perchlorate showed that though the loss of activity was more rapid, the total loss was less than with sodium chloride.[4] There was an apparent increase in rate above a degree of polymerization of 13, due to phase separation. In the absence of solid ammonium perchlorate, this phase separation takes place above a degree of polymerization of 35. It was predicted from the kinetic studies that the inclusion of ammonium perchlorate in a casting would necessitate an additional 1.6×10^{-4} mole of ferric acetylacetonate per equivalent of isocyanate above that required for binder alone. This was in good agreement with the catalyst concentration determined empirically in casting studies.

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[1] Aerojet Report No. 1281, 14 June 1957, p. 5 (Confidential).

[2] Aerojet Report No. 868, 17 September 1954, p. 37 (Confidential).

[3] Aerojet Report No. 1281, 14 June 1957, p. 6 (Confidential).

[4] Ibid., Figure 7; Figure 2 of this report (No. 1318).

From the standpoint of pot life, a falling catalyst activity is undesirable. An attempt was made to stabilize the catalytic activity by aging the catalyst in the presence of small quantities of ammonium perchlorate and diisocyanate. The result was a less active catalyst which still gave a falling rate of polymerization.[1]

c. Studies with Metal Salts and Complexes

The extraordinary catalytic activity of ferric acetylacetonate prompted the study of similar complexes of other metals. Of those tested, many were characterized by a serious partial loss of activity during the initial stages of the polymerization. These included the acetylacetonates of cerium^{III}, zirconium^{IV}, thorium^{IV}, and the dibenzoylmethane and the acetoacetic ester derivatives of copper^{II}.[2]

The acetylacetonates of beryllium^{II} and palladium^{II} had virtually no catalytic activity.[3] Aluminum acetylacetonate had a moderate catalyst constant (k_c) which increased with decreasing catalyst concentration. Related to this was the activity of sodium acetylacetonate, which was higher than would be predicted from its basic strength.[4] It is likely that part of the activity of the last two materials was derived from an exchange with metallic impurities in the system. In contrast, the acetylacetonates of beryllium^{II} and palladium^{II}, having extremely low dissociation constants, would not be expected to exchange appreciably.

The dibenzoylmethane chelate of iron^{III} (analagous to ferric acetylacetonate) was prepared, and its catalyst constant was determined. Its catalytic activity was slightly higher than that of ferric acetylacetonate.[5]

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[1] Aerojet Report No. 1281, 14 June 1957, p. 6 (Confidential).

[2] *Ibid*., p. 4; Aerojet Report No. 1241, 15 March 1957, p. 6 (Confidential).

[3] Aerojet Report No. 1241, 15 March 1957, p. 6 (Confidential).

[4] *Ibid*., p. 5.

[5] Aerojet Report No. 1281, 10 June 1957, p. 5 (Confidential).

The results from semi-quantitative tests have indicated that of the two, the dibenzoylmethane chelate is less affected by the presence of oxidizer. Its low dissociation constant, in comparison with that of ferric acetylacetonate,[1] suggests that a study of the more tightly bound ligands may be profitable.

Cobalt naphthenate and octyleneglycol titanate were shown to have low activities. In view of their low cost, they may find application where only moderate catalysis is required.[2]

The iron complex of 8-hydroxyquinoline and various metal chelates of disodium versenate were not sufficiently soluble in organic materials to be of interest. However, despite its insolubility, disodium versenate had some catalytic activity.[2]

The use of ferric acetonylacetonate as a catalyst has been mentioned in the literature.[3] However, no description of a metal derivative of acetonylacetone (2,5-hexanedione) could be found. A few attempts were made, unsuccessfully, to prepare this material in aqueous medium in a manner similar to that described for ferric acetylacetonate.

d. Studies with the Ferrocenes and β-Dicarbonyl Compounds

Several variations of the catalyst system (ferrocene plus a β-dicarbonyl compound) were investigated.[4] The system was noteworthy in that induction periods of from 1/2 to 1-3/4 hr were demonstrated.

Ferrocene, dimethylferrocene, acetylferrocene, and ferrocene-monocarboxylic acid were studied. Used alone, as catalysts, each of these materials developed a catalytic activity roughly one-tenth that of ferric acetylacetonate, with the dimethyl derivative displaying the longest induction period. The co-addition of a β-dicarbonyl compound (such as dibenzoylmethane, acetylacetone, ethyl acetoacetate or ethyl malonate) increased the catalytic

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[1] Chemistry of the Coordination Compounds, J. C. Bailar, Jr., Reinhold, 1956, p. 182.

[2] Aerojet Report No. 1241, 15 March 1957, p. 5 (Confidential).

[3] E. Kuhr, German Patent 919,071, 11 October 1954;
S. Petersen, Ann. 562, 206 (1949).

[4] Aerojet Report No. 1241, 15 March 1957, p. 7 (Confidential).

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activity, following the induction period, to approximately that of ferric acetylacetonate. The effectiveness decreased in the order named.

A detailed examination of the increase in catalysis suggested an autocatalytic conversion to a more active species, presumably involving an oxidation reaction by the nitro-groups in the monomers. In the absence of a β-diketone, this catalytic activity partially decayed, giving inflections in plots of degree of polymerization vs time.[1] In the presence of a β-diketone, this active intermediate was either stabilized or converted to a different active species.

In translating this catalyst system to propellant formulations, it was found that the surprisingly high catalyst concentration of 2 x 10^{-4} moles per equivalent of isocyanate was required with XIII-A-8X-0.6NPN binder (no oxidizer). However, a pot life of 2 hr was realized at room temperature, and a good cure was obtained. A control with ferric acetylacetonate required 1 x 10^{-5} mole per equivalent of isocyanate and had a pot life of 0.5 hour. Only partial cures could be obtained with XIII-H-8X binders, despite increased catalyst concentration and temperature of cure. No cure could be obtained in the XIII-A system, when oxidizer (ammonium perchlorate) was included in the formulation.[2]

e. The Effect of Copper Chromite in Polyurethane Castings

It was observed that the burning-rate catalyst, copper chromite, increased the rate of cure of polyurethane propellants. A kinetic study supported this observation (Figure 2, Curves I, II, III, and IV). The polymerization media contained 20 g (0.1 mol) of XIII-diisocyanate, 13.5 g (0.1 mol) of J-diol, and 20 g of solid ammonium perchlorate with sufficient dioxan to make a liquid volume of 200 ml. In the absence of catalyst, the rate of polymerization, k, was approximately 10^{-3}. Copper chromite (200 mg)

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[1] Ibid., Figures 10 through 15.

[2] Aerojet Report No. 1281, 14 June 1957, p. 9 (Confidential).

had a definite catalytic activity which decreased slowly with time (Curve III). With copper chromite (200 mg) in the presence of 200 mg of acetylacetone, the rate of polymerization was initially much less but rose slowly, approaching the value of copper chromite alone (Curve IV). Curves I and II, (Figure 2) compare the activity of 2×10^{-4} mol/liter of ferric acetylacetonate and that of the ferric acetylacetonate plus 200 mg of suspended copper chromite. In both cases, the rate of polymerization decreased with time, but a definite enhancement by the copper chromite was observed. This increase was greater than the additive effect of copper chromite alone.

f. Studies with Coded Catalysts

As a result of the screening program, 30 additional catalysts (Catalysts 101 through 130) were selected for further study.

The behavior of Catalysts 101 through 118 has been reported in detail.[1] Of these, Catalyst 108, 116, and 118 were too low in activity to warrant further interest. Catalysts 102, 112, 113, and 115, though of moderate-to-high activity, showed decided loss of catalytic activity during the course of polymerization. Of the remainder, Catalysts 101, 105, 106, 107, and 117 had essentially constant activity, whereas 103, 104, 109, 110, 111, and 114 increased in activity. Qualitative screening for "salt effect" eliminated Catalysts 106, 109, 110, and 111 on the basis of severe loss of activity. Catalysts 105 and 107, although severely affected by sodium chloride, were only mildly inactivated by ammonium perchlorate. Catalyst 103 is a hydrate (the most readily obtained form) of 104, tested as such in order to determine the desirability of the catalyst before attempting to obtain it in the anhydrous form. This catalyst, therefore, is of further interest only as Catalyst 104.

There remained seven materials of sufficient interest for further study (Catalysts 101, 102, 104, 105, 107, 114, and 117). Catalysts 101, 102, 105, 107, and 117 have not yet been studied in propellant formulations. Catalysts 101, 102, 105, and 107 are hydrates; hence means of drying them must first be found.

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[1] *Ibid.*, p. 6.

Catalyst 104 is characterized by having a catalytic activity at 50°C which increases slowly (over a period of several hours) from a low level to one comparable to that of ferric acetylacetonate.[1] Unlike ferric acetylacetonate, however, its activity is enhanced by the presence of sodium chloride or ammonium perchlorate. The increasing catalytic activity is believed to be due to an oxidation (by nitro groups) of the metallic portion of the catalyst. This was partially confirmed when the oxidized form (Catalyst 119) was obtained and shown, semi-quantitatively, to have a very high activity which was enhanced by the presence of oxidizer. The use of Catalyst 104 in a XIII-H-8X-0.4DNPNP binder formulation gave a good cure in 48 to 72 hr at 110°F, whereas Catalyst 119 gave a cure in about 24 hours. Catalysts 104 and 119 have thus far yielded only bubble-filled castings when employed in XIII-A formulations. It was observed that bubble formation occurred in the degassed XIII-A monomer system, after the addition of these catalysts. This bubbling continued throughout the remainder of the degassing period, despite extra precautions taken to thoroughly degas before adding the catalyst.

Catalyst 114 was used successfully in both XIII-A-8X-0.6NPN-69AP and XIII-H-8X-0.6NPN-69AP propellant castings.[2] Catalyst levels were 2.5×10^{-4} and 1×10^{-3} moles of Catalyst 114 per equivalent of isocyanate, respectively - the same concentrations as those required with ferric acetylacetonate. The pot life in each case was greater than that of the control casting employing ferric acetylacetonate. Thus it appears that Catalyat 114 can replace ferric acetylacetonate in applications in which maximum pot life is needed.

Catalysts 120 through 123 and 125 through 127 were selected for further study, primarily because of their low "salt effect" observed in the semi-quantitative tests. Catalysts 124, 128, 129, and 130 were selected for quantitative study because they appeared to have induction periods. Kinetic studies were carried out with Catalyats 121 (Figure 3, Curve IV;

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[1] *Ibid.*, Figures 10, 11, and 12.

[2] See also Aerojet Report No. 2795-1 (in press), Contract NOrd 16881, Development and Testing of Nitropolymer Propellants (Confidential).

Figure 4, Curves I and II), 122 (Figure 3, Curve I), 123 (Figure 3, Curve II), and 124 (Figure 3, Curve III). Catalyst 121 was studied kinetically in the presence of ammonium perchlorate (Figure 4, Curves III and IV). Catalysts 120 and 125 through 130 remain to be studied.

At several concentration levels, Catalyst 121 had an initial catalyst constant (k_c) of approximately 1×10^4 (for FeA_3, $k_c = 6 \times 10^5$), which in later stages increased to as high as 4×10^5. This rise was more pronounced at the higher catalyst concentrations. The presence of ammonium perchlorate resulted in a diminishing catalyst activity during the polymerization.

Because Catalysts 122 and 123 were not sufficiently soluble in dioxan to permit their addition as solutions, they were added as suspensions. The activity of each catalyst decreased with time. Catalyst 124 was essentially insoluble in dioxan, and an amount equal to 5.5×10^{-5} mole/liter was added as a solid to the polymerization medium. Complete solution was not obtained. An increasing rate of polymerization was noted during the first 0.75 hour. This may have been due to slow solubilization during this period. In qualitative tests employing more concentrated solutions of the monomers, this catalyst was readily soluble to the extent of at least 10^{-3} mole/liter.

g. The Reactivity of Polyglycidyl Nitrate

The rate of polyurethane formation from the reaction of XIII-diisocyanate with polyglycidyl nitrate (PGN) was studied, with ferric acetylacetonate as the catalyst.[1] From the rate at several temperatures, the activation energy was calculated to be 17,600 cal/mole. The reactivity of PGN is roughly 0.4 that of J-diol.

3. Summary and Evaluation

A number of catalysts have been discovered which show the "salt effect" to a minor degree or not at all. Since the salt effect is a

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[1] Aerojet Report No. 1241, 15 March 1957, p. 38 (Confidential).

major contributor to poor pot life, the use of these catalysts in propellant formulations should, as compared with ferric acetylacetonate, allow a longer casting time, or a more rapid cure with the same casting time. Some of these catalysts proved inapplicable to propellant use, whereas others remain to be evaluated in this regard.

Catalyst 114 has proved out well in general propellant applications, whereas Catalysts 104 and 119 have proved to be useful with one of the nitropolymer systems tested (XIII-H), but not with another (XIII-A). A real advantage of Catalyst 104 lies in its increase in activity during polymerization, although this is expected to be limited to formulations containing nitro compounds.

A series of delayed-action catalysts, the ferrocenes, proved useful with the XIII-A system but not with the XIII-H. These catalysts are ineffective in the presence of oxidizer.

Complete evaluation of other promising catalysts is expected to lead to additional, useful catalysts from which the one best suited to a given application may be selected.

4. Experimental

The quantitative studies were conducted as described in previous reports.[1] Descriptions of the screening test and of the technique for testing in the presence of ammonium perchlorate appear in a recent report.[2]

B. FORMULATION STUDIES

1. Introduction

As part of a continuing effort toward the development of resin binders for composite propellants, the polyurethane products formed from nitrodiisocyanates and long-chain diols are being investigated. Previous

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[1] Aerojet Report No. 590, 27 March 1952, p. 24 (Confidential);
Aerojet Report No. 868, 17 September 1954, p. 18 (Confidential).

[2] Aerojet Report No. 1281, 14 June 1957, p. 8 (Confidential).

reports have set forth the desirability of employing high-molecular-weight, high-energy diols in the preparation of nitropolyurethane propellants.[1] The desirable features are (a) the heat evolved (exotherm) during polymerization is diminished; (b) the shrinkage of the propellant mix during curing is reduced, thereby making case bonding more likely; and (c) a lower second-order-transition temperature (Tg) of the propellant can be obtained.

It is the purpose of this section to summarize the results obtained thus far with high-molecular-weight monomers and to describe the systematic research and development program which is being undertaken to exploit fully their potentialities.

2. Discussion

a. Epoxides

Three types of epoxides were studied in synthesizing long-chain energetic glycols. The nitrato diol, polyglycidyl nitrate (PGN), was easily prepared from glycidyl nitrate and was readily available for formulation studies.[2] A small quantity of the nitramino diol, poly-4-nitraza-1,2-epoxypentane (NEP), was prepared from the corresponding nitramino epoxide, but none of the nitro diols have been prepared in sufficient quantity and/or purity to allow complete evaluation. Trial polymerizations with impure 5,5-dinitro-2,3-epoxyhexane indicated that this material polymerized much more rapidly than 4-nitraza-1,2-epoxypentane, but that there was catalyst consumption.[3] Further polymerization studies will be conducted with 5,5-dinitro-2,3-epoxyhexane, when a material of higher purity becomes available. Kinetic studies were conducted on the polymerization of both glycidyl nitrate and 4-nitraza-1,2-epoxypentane initiated by ethylene glycol.[4] It has been reported that while acidic

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[1] Aerojet Reports No. 1119, 20 June 1956, p. 3 (Confidential); No. 1083, 19 March 1956, p. 11 (Confidential). Jet Propulsion Laboratory Progress Reports No. 20-264, 20-265, 15 July 1955 (Confidential).

[2] Aerojet Report No. 1202, 18 December 1956, p. 4 (Confidential).

[3] _Ibid._, p. 12.

[4] _Ibid._, p. 9.

catalysis (boron trifluoride) leads to some loss of hydroxylic end-groups, basic catalysis does not.[1] Both acidic and basic catalysts effected the polymerization of 4-nitraza-1,2-epoxypentane, although some darkening occurred with base. The deleterious action of the basic catalyst was more pronounced during the polymerization of glycidyl nitrate.[2]

b. Polyurethane Binders and Propellants Based on Long-Chain Diols

Prior work showed that the polymerization of PGN with 3-nitraza-1,5-pentane diisocyanate (XIII-diisocyanate) does not lead to a high-molecular-weight polyurethane and that this polyurethane requires at least 30 equiv % of the crosslinker, <u>tris</u>-(hydroxymethyl)-nitromethane (nib-glycerol, symbol X) in order to form an insoluble gel.[3] This indicated that the PGN was not completely bifunctional. In contrast, NEP readily formed insoluble gels with XIII-diisocyanate and nib-glycerol.[4] However, because of the high viscosity of the NEP binder mixture and the low specific impulse (which would require a high percentage of oxidizer for adequate impulse), it was questionable whether a practical casting system could be developed with this diol.[4]

Because PGN was the only readily available, high-energy, long-chain diol and because PGN (plus 30 equiv % nib-glycerol) does form a rubbery, acetone-insoluble nitropolyurethane with XIII-diisocyanate, work was continued on the utilization of this material in propellant formulations. The experience gained in this study will be of help in overcoming difficulties which

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[1] H. P. Drew and J. R. Schaeffer, <u>Chemicals From Petroleum</u>, a Symposium of the Division of Petroleum Chemistry of the American Chemistry Society, April 1956, p. 83.

[2] Aerojet Report No. 1202, 18 December 1956, p. 9 (Confidential).

[3] Aerojet Reports No. 119, 20 June 1956, p. 3; 1083, 19 March 1956, p. 11 (Confidential).

[4] Aerojet Report No. 1281, June 1957, p. 13 (Confidential).

will be encountered in the subsequent use of high-molecular-weight nitro and nitramino diols.

Castings incorporating PGN of molecular weight about 1000 were prepared without plasticizer and with various levels of plasticizer. The characterization of these XIII-PGN-30X propellants included visual observation of the samples and the determination of burning rates, densities, vacuum stabilities, storage stabilities, and transition temperatures.[1] Attempts to prepare castings incorporating PGN of higher molecular weights (up to 4000) failed. Acetone-insoluble gels could not be obtained.

The casting work with PGN-diol has been disappointing. The castings, which were successfully prepared, were not sufficiently crosslinked to behave as rubbers, nor were they thermally stable.[2] It is believed that this is due in part to the loss of hydroxyl end-groups in the preparation of the PGN. The preparation of PGN from glycidyl nitrate and a triol would be expected to lead to a high-molecular-weight triol contaminated (by the loss of hydroxyl groups) with some diol and with negligible amounts of monohydroxy and non-functional materials. The utilization of triol-initiated polyglycidyl nitrate of proper molecular weight should lead to a tough and flexible polyurethene binder for propellants. Such a triol (PGNT) was prepared by initiating the polymerization of glycidyl nitrate with trimethylol propane.[3] XIII-PGNT fuel-binder and propellant formulations were then prepared. A most significant improvement had occurred in the flexibility, resilence, and body of these propellants over that of the XIII-PGN-30X samples. The characterization of these XIII-PGNT specimens showed that they were more highly crosslinked than similar XIII-PGN-30X formulations. However, no improvement in thermal stability was indicated inasmuch as the vacuum stability gassing rates remained the same as

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[1] Aerojet Reports No. 1202, 18 December 1956, p. 3 (Confidential); No. 1241, 15 March 1957, p. 30 (Confidential).

[2] Aerojet Report No. 1202, p. 3; No. 1241, p. 30; No. 1281, p. 11 (Confidential).

[3] Aerojet Report No. 1281, 14 June 1957, p. 12 (Confidential).

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for the XIII-PGN-30X materials, although structural degradation did not occur until after 100 hr at 180°F, as compared with 24 hr for XIII-PGN-30X samples.[1]

c. Thermal Stability Studies

The instability of PGN and PGNT formulations may be due to the presence of small amounts of nitrous or nitric acids arising either from decomposition or as impurities in the glycidyl nitrate. It is believed that these acids enhance the rate of polyurethane degradation.[2] Consequently, a number of attempts were made to remove these impurities in order to improve stability. PGN and PGNT preparations were washed for 3 hr with a 5% aqueous solution of urea at 70°C, as recommended by the Jet Propulsion Laboratory.[3] Castings were prepared incorporating 1 wt% of nitric acid scavengers, such as ethyl centralite (N,N'-diethyl-N,N'-diphenyl urea) and magnesium oxide.

The effectiveness of the urea treatment on both PGN-diol and PGNT-triol was measured by vacuum-stability tests (Figures 5 and 6; Table 2). PGN-diol, treated with aqueous urea, exhibited a much lower rate of gas evolution than the untreated material. In time, however, the rates for both the treated and untreated PGN samples increased considerably. When this occurred, the apparatus was carefully checked for leaks, but none were found. The rates observed for PGNT-triol, treated and untreated, were low. The urea wash effected a slight improvement.

Binders and propellants that were stabilized by using urea-treated PGNT and by incorporating nitric acid scavengers showed little improvement in gassing rate over the unstabilized samples (Table 3; Figures 7 and 8). The sample which was stabilized with urea-washed PGNT and magnesium

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[1] Ibid., p. 13; Aerojet Report No. 1241, 15 March 1957, p. 33 (Confidential).

[2] Aerojet Report No. 5522-7, Aging of Polyurethane-Ammonium Nitrate Propellants, 27 November 1956 (Confidential).

[3] Jet Propulsion Laboratory Report No. 47, April 1955, p. 8 (Confidential).

oxide exhibited only a slight decrease in the 65.5°C gassing rate over the unstabilized sample (Figure 9). The gassing rate of this sample at 82.5°C was similar to that previously obtained from the unstabilized sample (Table 4; Figure 9).[1]

Storage-stability data were obtained on the previously prepared PGN and untreated PGNT binders and castings. The samples were stored, at ambient temperature, in a propellant shed. The highest recorded temperature in the shed was 110°F. After two and one-half months, the NPN-plasticized PGNT binders and castings had lost their three-dimensional structure and had completely liquefied; the DNPNP-plasticized (as well as the non-plasticized) PGNT binders and castings degraded in about 5 months. The observation that NPN-plasticized PGNT samples degraded first is similar to results obtained with PGN samples, wherein those samples plasticized with NPN degraded in about 2 weeks and the others degraded in about 6 weeks. From these studies, it is concluded that XIII-PGN and XIII-PGNT polymers are very susceptible to thermal decomposition.

d. Polyglycidyl Nitrate Initiated with *tris*-(Hydroxymethyl)-nitromethane

The polymerization of glycidyl nitrate, with *tris*-(hydroxymethyl)-nitromethane (instead of trimethylol propane) as the chain-initiating agent, would result in a triol (PGNX) of higher specific impulse than previously prepared polyglycidyl nitrates (PGN and PGNT). Although PGNX was not expected to solve the immediate problem of instability, its use in castings would lower oxidizer requirements and permit the utilization of larger percentages of stabilizers and ballistic additives; in addition, compatibility with existing nitroplasticizers should be enhanced.

An attempt to prepare PGNX of equivalent weight 500 (by the boron trifluoride-catalyzed polymerization of glycidyl nitrate in

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[1] Aerojet Report No. 1281 (Table 3; Figure 24), 14 June 1957 (Confidential).

methylene chloride solution, with nib-glycerol as chain initiator) was unsuccessful. The nib-glycerol proved to be insoluble in the methylene chloride, to the extent that the lowest equivalent weight was about 1200. This triol failed to form an acetone-insoluble gel with the XIII-diisocyanate, although a high concentration of ferric acetylacetonate and an extended cure time were employed. These results were similar to those obtained previously with PGNT of approximately the same molecular weight (1500).[1] The procedure for the preparation of polyglycidyl nitrate, initiated with <u>tris</u>-(hydroxymethyl)-nitromethane, was the same as that used in preparing PGN.[2] About one-half of the nib-glycerol failed to dissolve in the methylene chloride.

e. Nitroepoxy Resin Formulations

Preliminary studies with 4-nitraza-1,2-epoxypentane indicated that flexible, crosslinked polymers could be obtained by the copolymerization of a high-energy monoepoxide with a small amount of a diepoxide.[3]

III. TECHNICAL PROGRESS: ORGANIC SYNTHESES

A. PREPARATION OF NITRO OLEFINS

1. Introduction

During the past year, a portion of the organic synthesis work was concerned with attempts to improve (from the standpoint of economy and/or safety) the preparations of 4-nitraza-1-pentene, 5,5-dinitro-2-hexene, 5,5,5-trinitro-2-pentene, and 4,4-dinitro-1-pentene. The olefins were desired as intermediates in the syntheses of the corresponding epoxides, which, in turn, were desired for subsequent polymerization to high-molecular-weight diols (see paragraph II,B). A number of the olefin syntheses continue to have serious disadvantages, but extensive process-improvement studies must be deferred until warranted by successful utilization of the corresponding epoxides.

2. 4-Nitraza-1-pentene

4-Nitraza-1-pentene was desired as an intermediate for the

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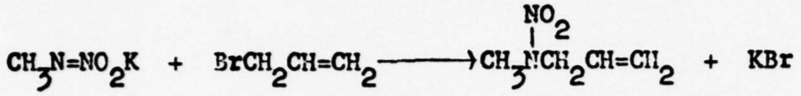
[1] *Ibid.*, p. 12.

[2] Aerojet Report No. 1022, 18 December 1956, p. 4 (Confidential).

[3] Aerojet Report No. 1281, 14 June 1957, p. 13 (Confidential).

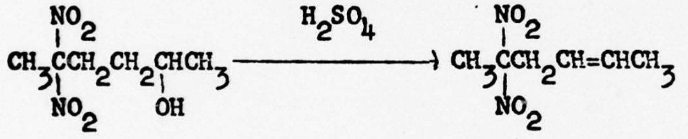
preparation of 4-nitraza-1,2-epoxypentane. The preparation of the olefin from methylnitramine and allyl bromide was described.[1] Attempts to utilize allyl chloride rather than the corresponding bromide resulted in appreciably reduced yields of the olefin.[2]



$$CH_3N{=}NO_2K + BrCH_2CH{=}CH_2 \longrightarrow CH_3\overset{NO_2}{\overset{|}{N}}CH_2CH{=}CH_2 + KBr$$

3. 5,5-Dinitro-2-hexene

Interest in the polymerization of 5,5-dinitro-2,3-epoxyhexane necessitated the preparation of 5,5-dinitro-2-hexene.[3] To avoid the safety hazard attending the sulfuric acid dehydration of 5,5-dinitro-2-hexanol, 26 small-batch runs were made to obtain 156 g (53% yield) of the desired olefin (b.p. 63-66°C/0.5-1mm; n_D^{25} 1.4567).[4] An attempt to carry out the sulfuric acid dehydration in the presence of Ansul ether as a solvent was unsuccessful.[5]



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow{H_2SO_4} CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH{=}CHCH_3$$

4. 5,5,5-Trinitro-2-pentene

a. Discussion

The preparation of 5,5,5-trinitro-2,3-epoxypentane, desired for polymerization studies, required larger quantities of 5,5,5-trinitro-2-pentene than were heretofore available. The original dehydration with concentrated sulfuric acid proved to be hazardous.[6]

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[1] Aerojet Report No. 1119, 20 June 1956, p. 15 (Confidential).

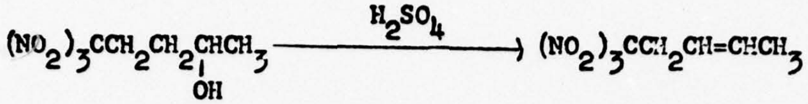
[2] Aerojet Report No. 1202, 18 December 1956, p. 18 (Confidential).

[3] Aerojet Report No. 638, 7 October 1952, p. 76 (Confidential).

[4] Aerojet Report No. 1202, 18 December 1956, p. 20 (Confidential).

[5] Aerojet Report No. 1241, 15 March 1957, p. 46 (Confidential).

[6] Aerojet Report No. 590, 27 March 1952, p. 60 (Confidential).



$$(NO_2)_3CCH_2CH_2\underset{OH}{CH}CH_3 \xrightarrow{H_2SO_4} (NO_2)_3CCH_2CH{=}CHCH_3$$

Fair yields (35-45%) of the olefin were obtained by heating 5,5,5-trinitro-2-pentanol with polyphosphoric acid (at 110-120°C) for 5 to 10 minutes. A crude yield of 50% was obtained by adding the alcohol to polyphosphoric acid at 145-150°C (and at 1-mm pressure) so that olefin was removed as it formed. However, material obtained in these procedures yielded, upon standing, an unidentified white solid, and thus complicated isolation of the olefin.[1] The vacuum technique was effectively applied to the dehydration with concentrated sulfuric acid; the pure product was more readily obtained in yields of 38%.[2]

More recently, several runs were made on a 0.1-mole scale. Although previous reaction conditions were closely duplicated, the yields of crude product did not exceed 13%. The lower yields obtained during these preparations were possibly caused by an inferior starting material. It was noted that the alcohol had a refractive index of 1.4632 at the time of use, whereas a value of 1.4673 had been found at the time of preparation approximately 6 months before. The determination of the reason for this change in the alcohol was not investigated.

b. Experimental

Five runs were made, of which the following was typical. Twenty-two and three-tenths grams (0.10 mole) of 5,5,5-trinitro-2-pentanol (n_D^{24} 1.4632) was added dropwise to 90 ml of concentrated sulfuric acid, heated at 130 ± 10°C; the entire system was maintained at a pressure of 1 to 1.5 mm, by means of a vacuum pump. The addition time was 2 hr, and the olefin, which distilled as it was formed, was collected in a receiver submerged in an ice bath. At the completion of the reaction, the crude product was dissolved in

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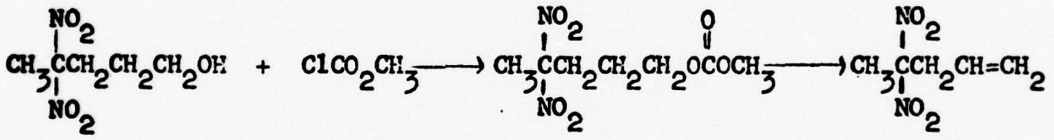
[1] Aerojet Report No. 1202, 18 December 1956, p. 22 (Confidential); Aerojet Report No. 1241, 15 March 1957, p. 44 (Confidential).

[2] Ibid., p. 46.

20 ml of hexane, and the hexane solution was washed three times with 25-ml portions of water and then dried over sodium sulfate. The hexane was subsequently removed from the dried solution by evaporation under reduced pressure at room temperature. A pale-yellow oil remained which weighed 2.7 g (13%); n_D^{24} 1.4597 (pure olefin, n_D^{25} 1.4612).

5. <u>4,4-Dinitro-1-pentene</u>

4,4-Dinitro-1-pentene was sought as an intermediate for the preparation of 4,4-dinitro-1,2-epoxypentane. Attempts to prepare the pentene from 4,4-dinitro-1-pentyl acetate, by pyrolysis, failed.[1] Because it was reported that the pyrolysis of methyl carbonate esters occurs at somewhat lower temperatures than does the pyrolysis of the corresponding acetates,[2] 4,4-dinitro-1-pentyl methyl carbonate[3] was prepared by the reaction of 4,4-dinitro-1-pentanol and methyl chloroformate, using the procedure described in the literature.[2] The pyrolysis of the ester to the desired 4,4-dinitro-1-pentene has not been attempted.



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OH + ClCO_2CH_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OCOCH_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH{=}CH_2$$

B. PREPARATION OF NITRO EPOXIDES

1. <u>Introduction</u>

The currently available nitropolyurethanes have certain disadvantages which limit their application as propellant binders. The major problems are encountered in the actual formation of the nitropolyurethanes, during which a high-polymerization exotherm and a correspondingly short pot life are experienced. These inherent disadvantages stem from the low molecular weight of the monomers, particularly the nitro diols, which are now employed in nitropolyurethane production .

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[1] Aerojet Report No.1119, 20 June 1956, p. 17 (Confidential).

[2] Bailey and Hewitt, <u>J. Org. Chem.</u>, <u>21</u>, 543 (1956).

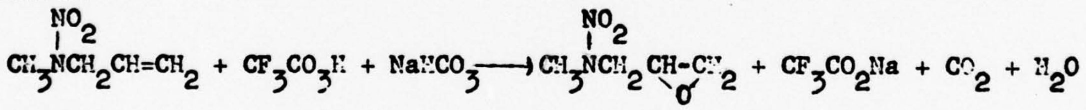
[3] Aerojet Report No. 1202, 18 December 1956, p. 24 (Confidential).

Assuming that the use of high-molecular-weight monomers will eliminate the indicated problems, the organic synthesis portion of the nitropolymer program was exclusively concerned with attempts to develop, during the past year, nitro diols or polyhydroxy nitro compounds of high molecular weight. Major emphasis was placed on the synthesis and purification of nitroepoxides which offer a convenient route to high-molecular-weight nitrodiols, on polymerization.

New epoxides which were prepared included 5,5-dinitro-1,2-epoxyhexane and 5,5,5-trinitro-2,3-epoxypentane. Attempts were also made to improve the syntheses of 4-nitraza-1,2-epoxypentane, 5,5-dinitro-2,3-epoxyhexane, and glycidyl 4,4,4-trinitrobutyrate, with extensive work being performed on the development of purification procedures for the last two compounds.

2. 4-Nitraza-1,2-epoxypentane

Early efforts to prepare 4-nitraza-1,2-epoxypentane from 4-nitraza-1-pentene by reaction with perbenzoic acid were not completely satisfactory because of the low order of reactivity of the olefin with this reagent.[1] The preparation of the epoxide utilizing trifluoroperacetic acid[2] in the presence of the buffers, sodium carbonate, sodium bicarbonate, and disodium hydrogen phosphate, was investigated and found to be preferable to the earlier method; best results were obtained with sodium bicarbonate as the buffer.[3]



$$CH_3\overset{NO_2}{\overset{|}{N}}CH_2CH{=}CH_2 + CF_3CO_3H + NaHCO_3 \longrightarrow CH_3\overset{NO_2}{\overset{|}{N}}CH_2\underbrace{CH{-}CH_2}_{O} + CF_3CO_2Na + CO_2 + H_2O$$

3. 5,5-Dinitro-1,2-epoxyhexane

a. Discussion

A method was sought to prepare sufficient quantities of 5,5-dinitro-1,2-epoxyhexane, in a high state of purity, for subsequent

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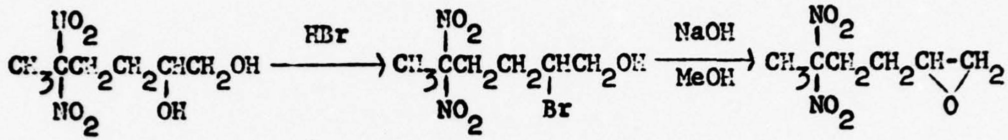
[1] Aerojet Report No. 1119, 20 June 1956, p. 22 (confidential).

[2] Emmons and Pagano, J. Am. Chem. Soc. 77, 89 (1955).

[3] Aerojet Report No. 1202, 18 December 1956, p. 26 (Confidential).

polymerization studies. The reaction sequence, represented below, involved (1) preparation of a bromohydrin from 5,5-dinitro-1,2-hexanediol and hydrobromic acid and (2) reaction of the bromohydrin with methanolic sodium hydroxide to yield the epoxide.[1,2]



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{OH}{CH}CH_2OH \xrightarrow{HBr} CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{Br}{CH}CH_2OH \xrightarrow[MeOH]{NaOH} CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{\diagdown O \diagup}{CH\text{-}CH_2}$$

Purification of this material proved to be a major problem. From a crude reaction product containing approximately 30% epoxide, small quantities of 82% material were obtained by distillation.[2,3] Using the distilled product, epoxide of 92% purity was obtained by a chromatographic procedure which employed two passes with an amount of absorbent (neutral alumina) equal to about 1.5 times the weight of the epoxide sample.[4] The chromatographic method, however, effected no further improvement in the purity of the crude reaction product.

b. Experimental[5,6]

The chromatographic procedure for the purification of the epoxide was performed as follows:

A 9.5-g sample of 85% (once-chromatographed) 5,5-dinitro-1,2-epoxyhexane was dissolved in 20 ml of "refrigeration grade" methylene chloride and passed onto a column packed with 15 g of alumina.

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[1] Ibid., p. 30.

[2] Aerojet Report No. 1241, 15 March 1957, p. 48 (Confidential).

[3] Aerojet Report No. L831-100, 15 April 1957, p. 3 (Confidential).

[4] Aerojet Report No. L831-102, 14 June 1957, p. 4 (Confidential).

[5] Aerojet Report No. 1202, 18 December 1956, p. 31 (Confidential).

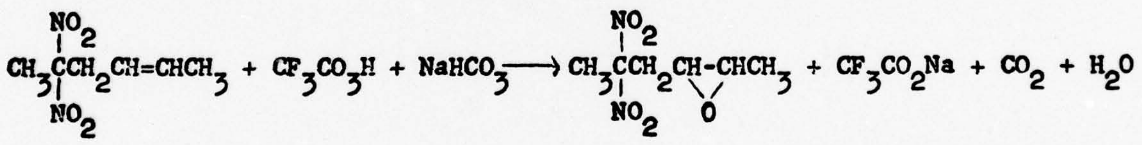
[6] Aerojet Report No. 1241, 15 March 1957, p. 51 (Confidential).

(Bio-Rad analytical grade chromatographic alumina, 100-200 mesh, washed with methylene chloride prior to use.) The liquid which passed through the column in this process was Fraction 1 and, upon evaporation of the methylene chloride, this liquid was found to contain no residual material. Additional methylene chloride was added, and Fraction 2 of 30 ml was collected, followed by Fraction 3 of 25 ml. Twenty-five milliliters of 1% ethanol in methylene chloride was next passed through the column and was collected as Fraction 4. Finally, 5% ethanol was used and 25 ml of solution was collected as Fraction 5. Upon evaporation of the solvent, Fraction 2 yielded 7 g of a pale-yellow oil which analyzed 93% epoxide. Fraction 3 contained 1.7 g of material which was not further tested, whereas Fractions 4 and 5 contained very small amounts of an oil of deeper color.

4. 5,5-Dinitro-2,3-epoxyhexane

a. Discussion

5,5-Dinitro-2,3-epoxyhexane was desired for polymerization investigations. It was prepared by the reaction of 5,5-dinitro-2-hexene and trifluoroperacetic acid in the presence of sodium bicarbonate, which served as a buffer.[1]



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2CH{=}CHCH_3 + CF_3CO_3H + NaHCO_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\underset{O}{CH{-}CH}CH_3 + CF_3CO_2Na + CO_2 + H_2O$$

The material so obtained was not sufficiently pure for polymerization studies. Although the product was improved by distillation, material of only 90% purity was obtained. On a small scale, passing a 5% solution of the epoxide (5 g) in methylene chloride through a neutral aluminum oxide (5 g) column gave a pure product.[2] Subsequently, this procedure proved inadequate when a larger

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[1] Aerojet Report No. 1119, 20 June 1956, p. 20 (Confidential).

[2] Aerojet Report No. 1831-101, 16 May 1957, p. 2 (Confidential).

amount (35 g) of epoxide was used.[1] Somewhat similar results were obtained from a procedure involving actual adsorption of the epoxide on alumina (in two to three times the amount previously employed), followed by elution with methylene chloride. For example, on a 10-g scale, this procedure increased the epoxide content from 91 to 98.5%, with a 70% recovery, whereas an attempt to purify 15 g of product in the same fashion gave two fractions of 94.5% purity (62% recovery) and 95.0% purity (25% recovery), respectively. From the available data, it must be concluded that this chromatographic purification, in its present state of development, is highly irreproducible.

Although it was previously suggested that the unverified storage instability of 5,5-dinitro-2,3-epoxyhexane was a complicating factor in its purification,[2] this epoxide has been shown to be a stable material. Thus, a sample which showed an original assay of about 91% gave identical values of 91.6% in duplicate analyses after 6 weeks' storage at 0°C and duplicate assays of 91.8 and 92.4% after storage for an additional week at ambient temperature.

b. Experimental[3]

Ten grams of 5,5-dinitro-2,3-epoxyhexane (91%) was dissolved in 10 ml of methylene chloride and put onto a column packed with 30 g of neutral alumina. The liquid which passed through during this process was collected as Fraction 1 and was found to contain no residual material upon evaporation of the methylene chloride. The column was then eluted with methylene chloride, and five 50-ml fractions were collected. Fraction 2 contained 7 g of a pale-yellow oil which gave duplicate epoxide analyses of 98.5% and 98.4%. Fraction 3 contained 2.2 g of material with an epoxide analysis of 96.2%. Fractions 4,5, and 6 contained very small amounts of oil which were not further investigated.

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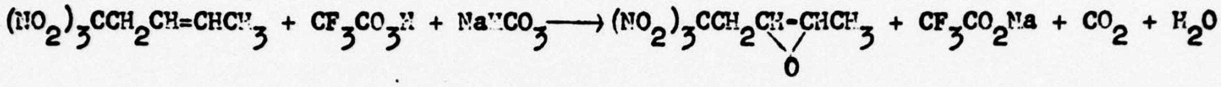
[1] Aerojet Report No. 1831-102, 14 June 1957, p. 4 (Confidential).
[2] *Ibid.*
[3] Aerojet Report No. 119, 20 June 1956, p. 20 (Confidential).

5. 5,5,5-Trinitro-2,3-epoxypentane

An initial attempt to prepare 5,5,5-trinitro-2,3-epoxypentane by the epoxidation of 5,5,5-trinitro-2-pentene with trifluoroperacetic acid was unsuccessful.[1] When the reaction time was prolonged, a low yield of a crude product was obtained.[2]



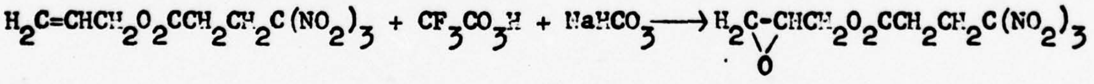
$$(NO_2)_3CCH_2CH{=}CHCH_3 + CF_3CO_3H + NaHCO_3 \longrightarrow (NO_2)_3CCH_2\underset{O}{CH{-}CH}CH_3 + CF_3CO_2Na + CO_2 + H_2O$$

Distillation gave material of only 77% purity. On a 1-g scale, chromatographic purification of a 5% solution on 1.5 g of neutral alumina yielded a product of 92% purity.[3] Experimental details have been described.[4]

6. Glycidyl 4,4,4-Trinitrobutyrate

a. Discussion

On the assumption that polymerization of the epoxide would lead to a diol of adequate molecular weight for incorporation in nitropolyurethane formulations, the synthesis of glycidyl 4,4,4-trinitrobutyrate[5] was undertaken to provide the quantity of material needed for polymerization studies. Epoxidation of allyl 4,4,4-trinitrobutyrate with trifluoroperacetic acid, in the presence of sodium bicarbonate as a buffer, yielded products which analyzed ca. 65% of the desired material.



$$H_2C{=}CHCH_2O_2CCH_2CH_2C(NO_2)_3 + CF_3CO_3H + NaHCO_3 \longrightarrow H_2\underset{O}{C{-}CH}CH_2O_2CCH_2CH_2C(NO_2)_3$$

$$+ CF_3CO_2Na + CO_2 + H_2O$$

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[1] Aerojet Report No. 1241, 15 March 1957, p. 53 (Confidential).

[2] Aerojet Report No. L831-101, 16 May 1957, p. 3 (Confidential).

[3] Aerojet Report No. L831-102, 14 June 1947, p. 4 (Confidential).

[4] Aerojet Report No. 1281, 14 June 1957, p. 20 (Confidential).

[5] Aerojet Report No. 563, 31 December 1951, p. 80 (Confidential).

Purification by means of the benzene solvate gave a 70% recovery of material which analyzed 80 to 90% epoxide. Although chromatographic treatment on 1.5 times the weight of neutral alumina was effective in obtaining a 100% product from 97% material when used on a small scale (1.5 g),[1] this purification procedure did not prove adequate when adapted to larger quantities (22 g) of less pure material.

b. Experimental[2]

Twenty-two grams of 81% glycidyl 4,4,4-trinitrobutyrate was dissolved in 25 ml of methylene chloride, and the solution was allowed to pass through a column packed with 32 g of neutral alumina. The effluent, which was Fraction 1, was found to possess no residual material after evaporation of the methylene chloride. More methylene chloride was added to the column, and three 50-ml fractions were collected. Fifty milliliters of 1% ethanol was added to the column and collected as Fraction 5. Fraction 2 contained 19.7 g of a yellow oil which analyzed 76% epoxide. Fractions 3, 4, and 5 contained small amounts of oil which were not further investigated.

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[1] Aerojet Report No. L831-102, 14 June 1957, p. 4 (Confidential).

[2] Aerojet Report No. 563, 31 December 1951, p. 80 (Confidential).

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TABLE 1

COMPARISON OF RATES OF FeA_3-CATALYZED POLYMERIZATIONS OF VARIOUS BATCHES OF XIII-DIISOCYANATE WITH J-DIOL

Conditions: Monomer end-group concentration 1.00 N in dioxan at 50°C

XIII Run No.	FeA_3 conc. mole/liter	k	k_c
31	1.1×10^{-5}	0.015	1.4×10^{3}
	2.5×10^{-5}	0.086	3.4×10^{3}
32	2.5×10^{-5}	3.5	1.4×10^{5}
	5.0×10^{-5}	7.4	1.5×10^{5}
AHS-1	1.1×10^{-5}	6.4	5.8×10^{5}
	2.5×10^{-5}	16.0	6.4×10^{5}
AHS-2	None	0.005	--
	1.0×10^{-5}	1.0	1.0×10^{5}

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TABLE 2

VACUUM STABILITY OF PGN DIOL AND PGNT TRIOL AT 82.5°C

Sample	Duration, hr	Rate, ml gm^{-1} hr^{-1}
PGN (Batch 66215) untreated	100	0.0140
PGN (Batch 66215) urea-washed	140	0.0022
PGNT (Batch 72492) untreated	200 +	0.0072
PGNT (Batch 72492) urea-washed	200 +	0.0053

TABLE 3

VACUUM-STABILITY GASSING RATES AT 65.5°C

Sample	ml $gm^{-1}hr^{-1}$	Duration of test, hr	Cure time at 110°F, hr
XIII-PGNT (urea-washed) -FeA_3(1×10^{-3})	.0057	200 +	160
XIII-PGNT (untreated) -FeA_3(1×10^{-3})	.0089	200 +	160
XIII-PGNT (urea-washed) -FeA_3(1×10^{-3}) 1% ethyl centralite	.0086	200 +	160
XIII-PGNT (urea-washed) -FeA_3(7×10^{-3}) 1% FC-15	.0183	200 +	160
XIII-PGNT (untreated) -66AP-FeA_3(5×10^{-3})	.0043	200 +	160
XIII-PGNT (urea-washed) -66AP-FeA_3 (1×10^{-3}) 1% MgO	.0021	200 +	136

TABLE 4

VACUUM-STABILITY GASSING RATES AT 82.5°C

Sample	ml $gm^{-1}hr^{-1}$	Duration of test, hr	Cure Time at 110°F, hr
XIII-PGNT (urea-washed) -66AP-FeA_3 (1×10^{-3})-1% MgO	.0234	200 +	136
*XIII-PGNT (untreated) -66AP-FeA_3 (1×10^{-3})	.0200	200 +	90

---

*See Table, Aerojet Report No. 1281, 14 June 1957 (Confidential).

TABLE 5

NOMENCLATURE USED IN SUMMARY AND SECTION II

XIII - 3-Nitraza-1,5-pentane diisocyanate

A - 2,2-Dinitro-1,3-propanediol

J - 2-Methyl-2-nitro-1,3-propanediol

X - <u>tris</u>(Hydroxymethyl)-nitromethane

H - 5,5,5-Trinitro-1,2-pentanediol

PGN - Polyglycidyl nitrate, diol initiated

PGNT - Polyglycidyl nitrate, triol initiated

NPN - 4-Nitrazapentanonitrile

DNPNP - 2,2-Dinitropropyl 4-nitrazapentanoate

NEP - 4-Nitraza-1,2-epoxypentane

AP - Ammonium perchlorate; 70% slow-speed grind, 30% high-speed grind

Cu 0202 - Copper chromite, supplied by Harshaw Chemical Co.

k is the rate constant in the equation $DP = 1 \times kc_0t$, i.e., the slope of a plot of degree of polymerization vs time.

k_c is k divided by the concentration of the catalyst.

FORMULATIONS

In XIII-PGNT-0.2NPN-68AP-$FeA_3(1 \times 10^{-3})$

XIII is 3-nitraza-1,5-pentane diisocyanate.

PGNT is polyglycidyl nitrate with a molecular weight of about 1500, initiated with trimethylolpropane.

0.2NPN is 4-nitrazapentononitrile/binder in a weight ratio of 0.2, where the binder is XIII-PGNT.

68AP is ammonium perchlorate in 68% of total propellant weight.

$FeA_3(1 \times 10^{-3})$ is ferric acetylacetonate in a concentration of 1×10^{-3} mol per equivalent of isocyanate.

In XIII-PGN-30X-$FeA_3(8 \times 10^{-3})$

PGN is polyglycidyl nitrate of molecular weight about 1000, initiated with ethylene glycol.

30X is 30 equivalent % <u>tris</u>-(hydroxymethyl)-nitromethane.

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RATE OF POLYMERIZATION OF XIII-J*, 1 N IN DIOXAN
AT 50°C WITH FERRIC ACETYLACETONATE

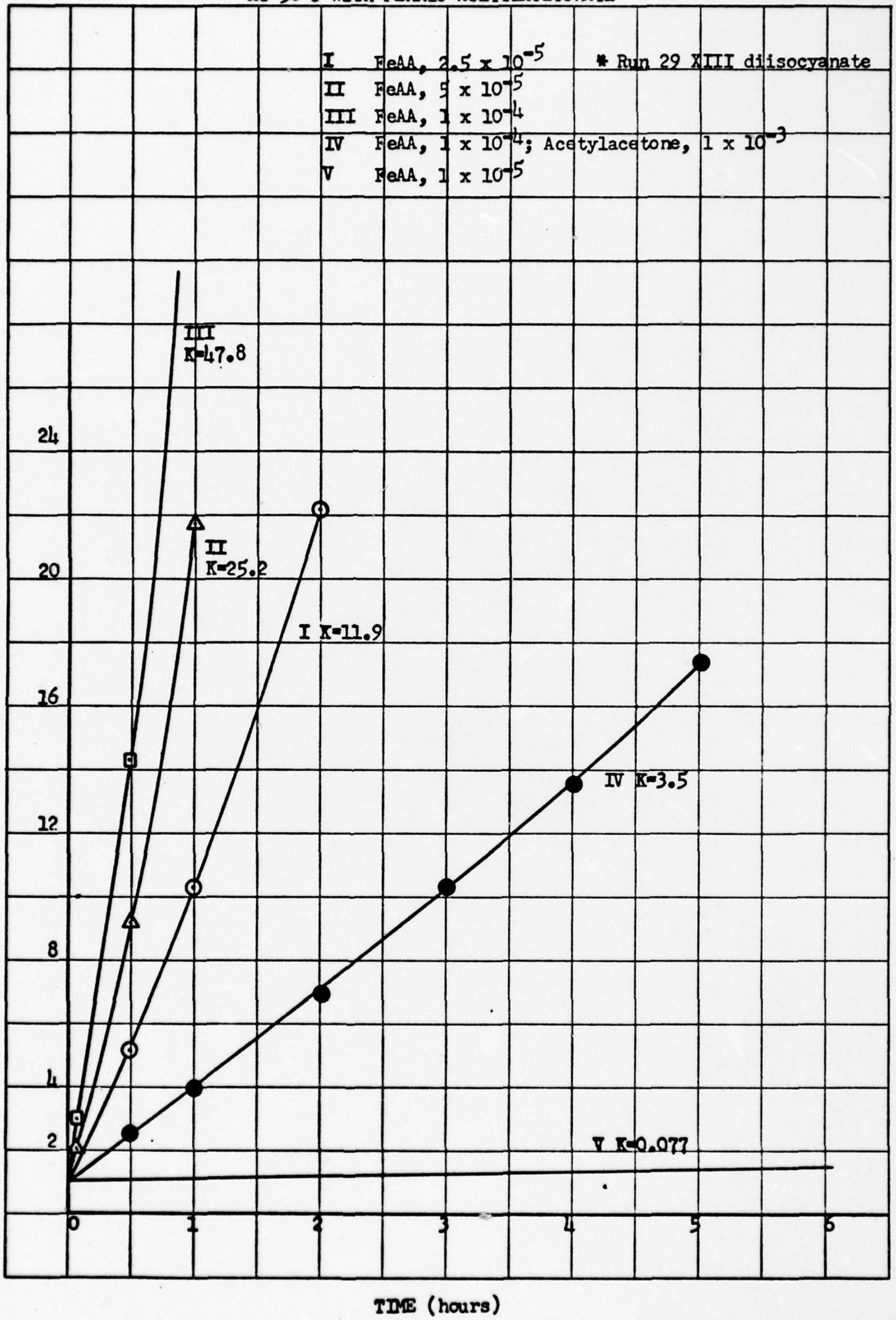

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Figure 1

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RATE OF POLYMERIZATION OF XIII-J, 1 N IN DIOXAN AT 50°C
IN PRESENCE OF SOLID AMMONIUM PERCHLORATE

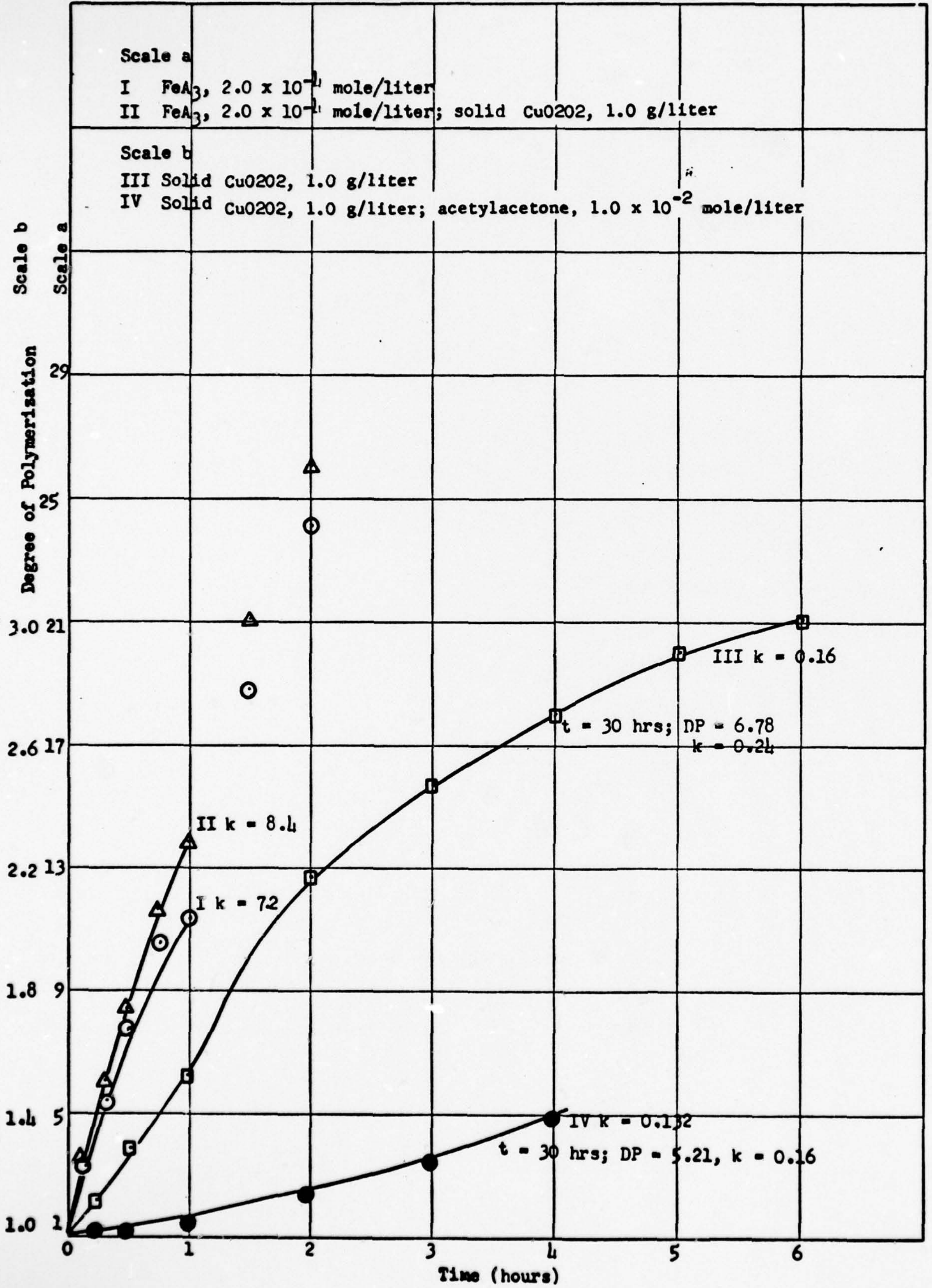

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Figure 2

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RATE OF POLYMERIZATION OF XIII-J, 1 N IN DIOXAN AT 60°C WITH VARIOUS CATALYSTS

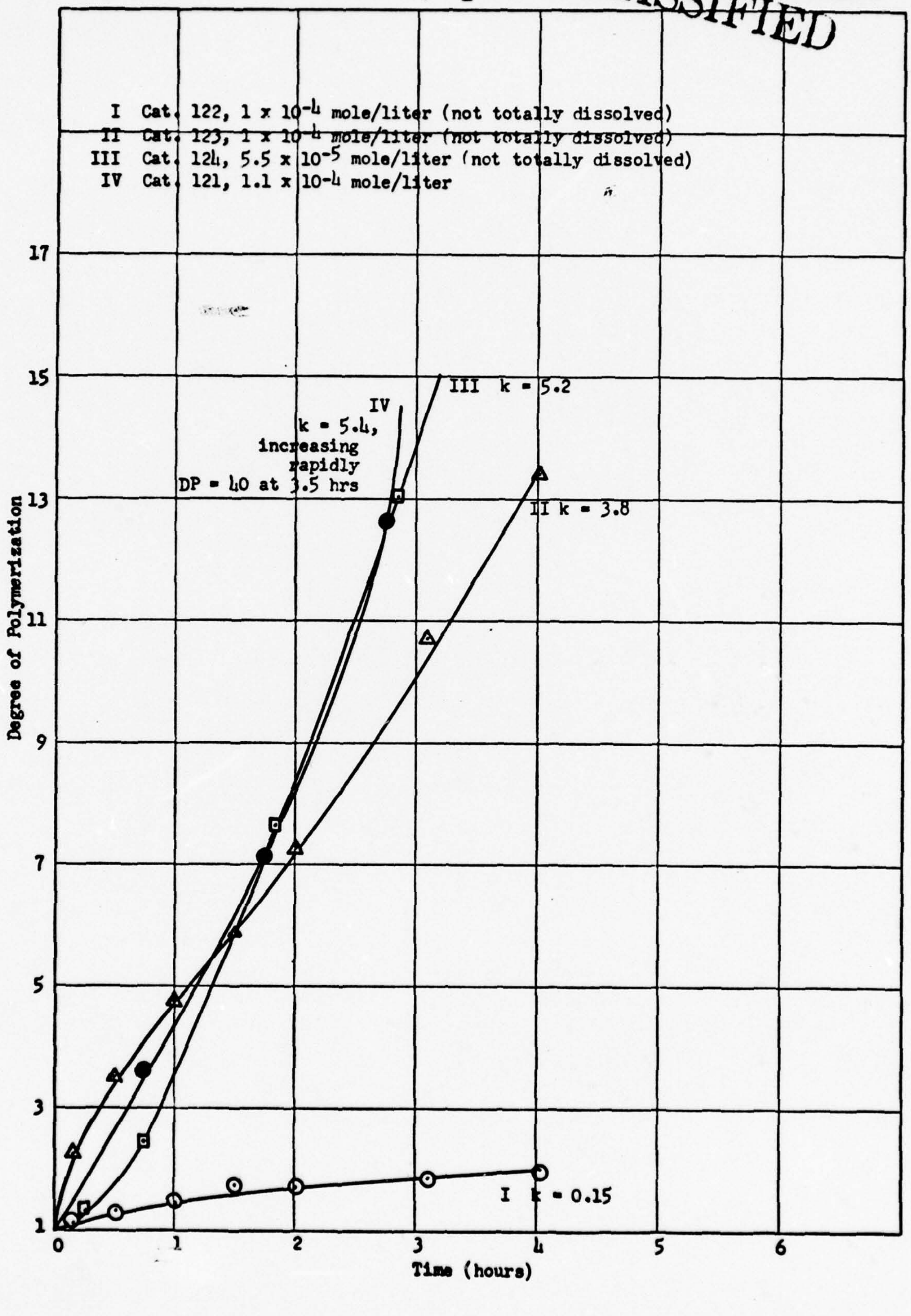

Figure 3

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RATE OF POLYMERIZATION OF XIII-J, 1 N IN DIOXAN AT 50°C WITH CATALYST 121

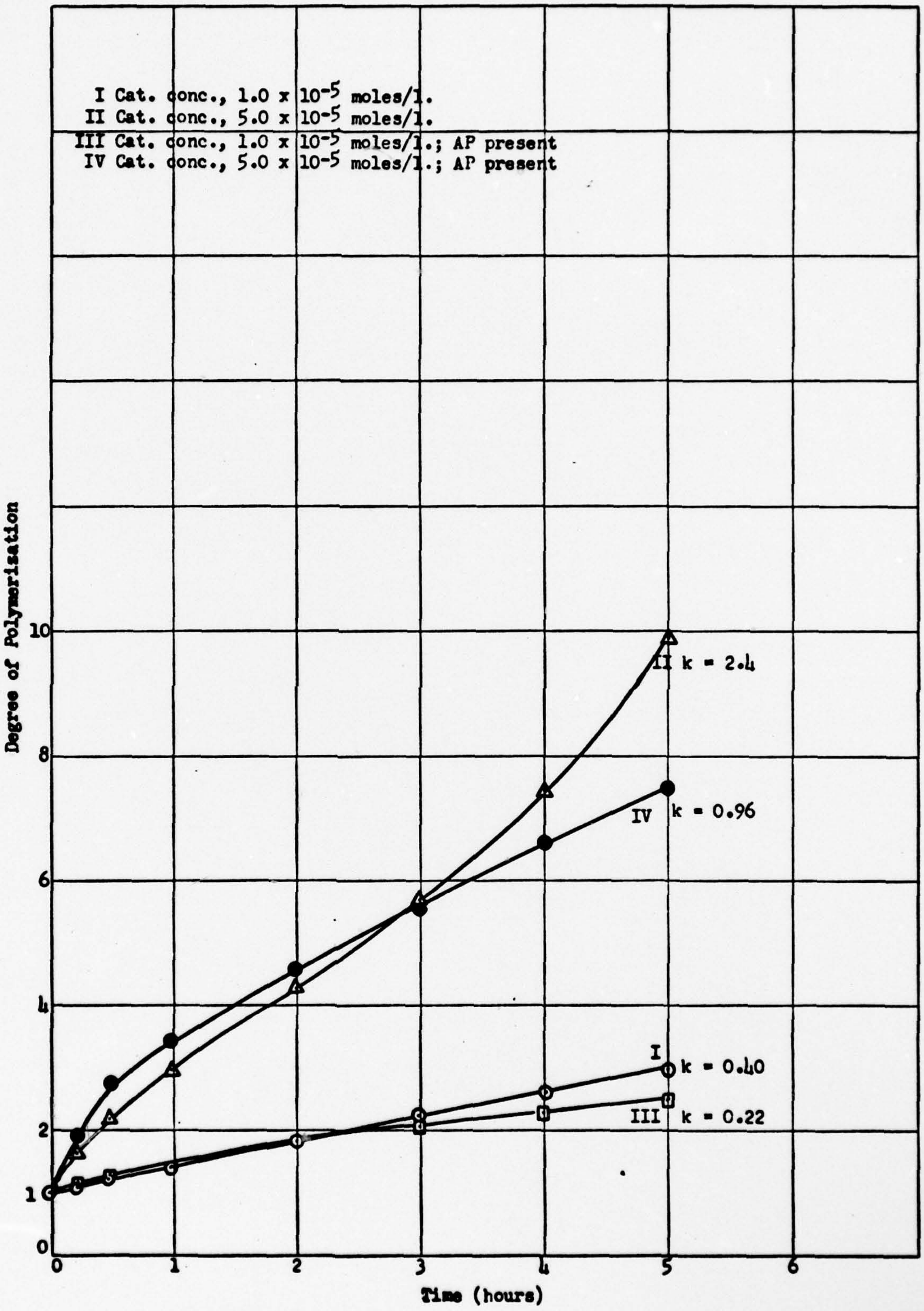

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Figure 4

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VACUUM STABILITY OF PGN DIOL AT 82.5°C

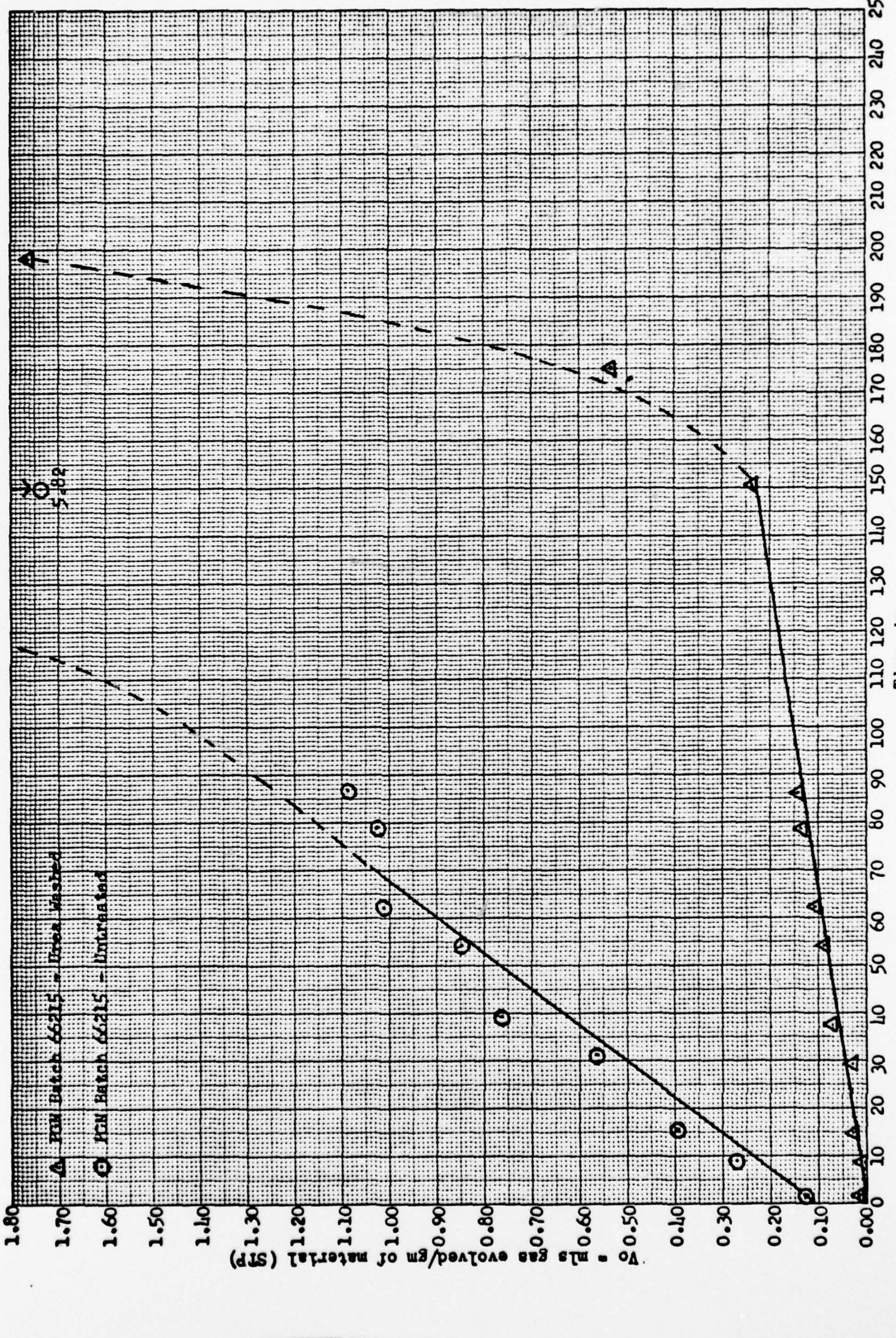

Figure 5

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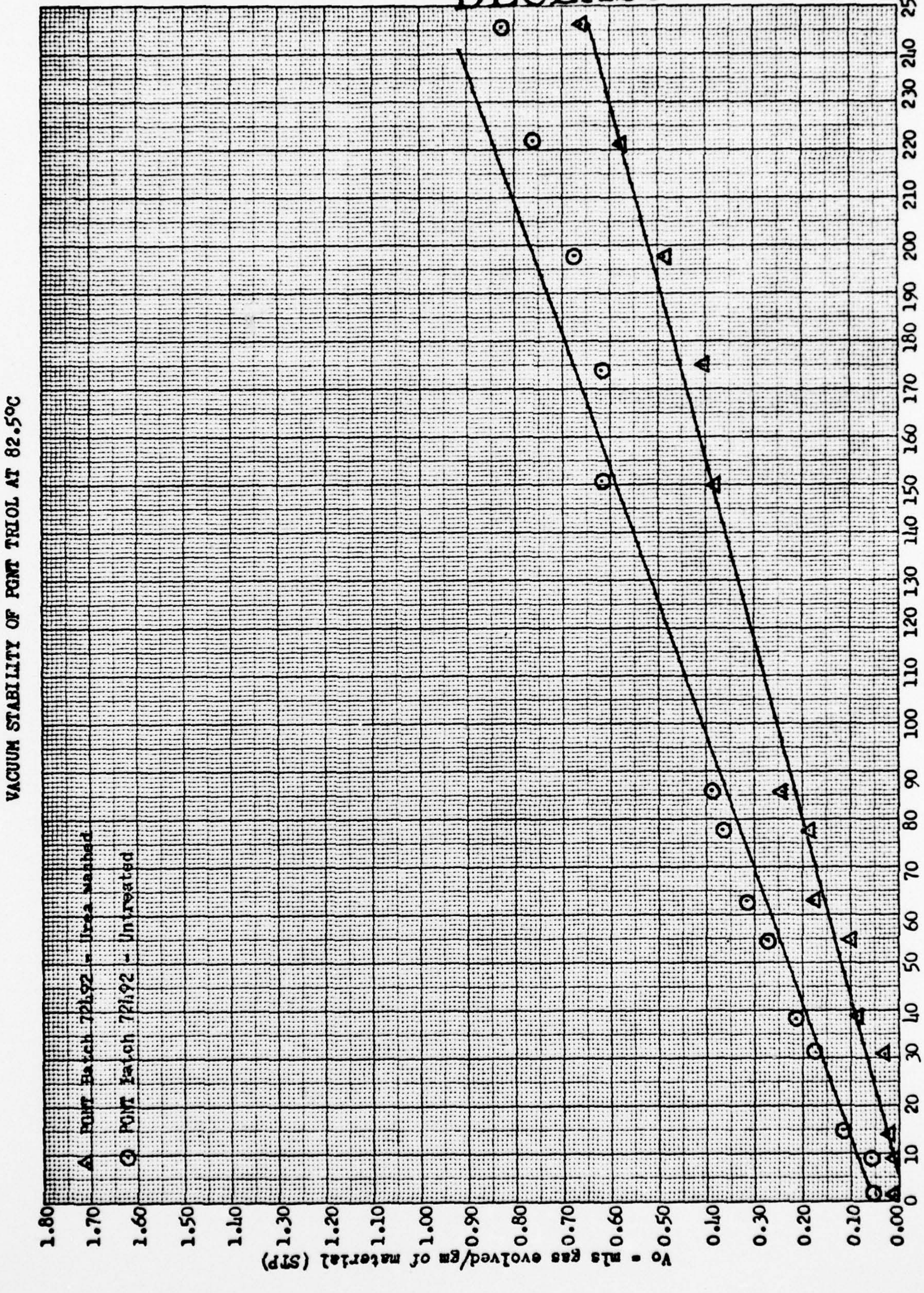
VACUUM STABILITY OF PGNT TRIOL AT 82.5°C

Figure 6

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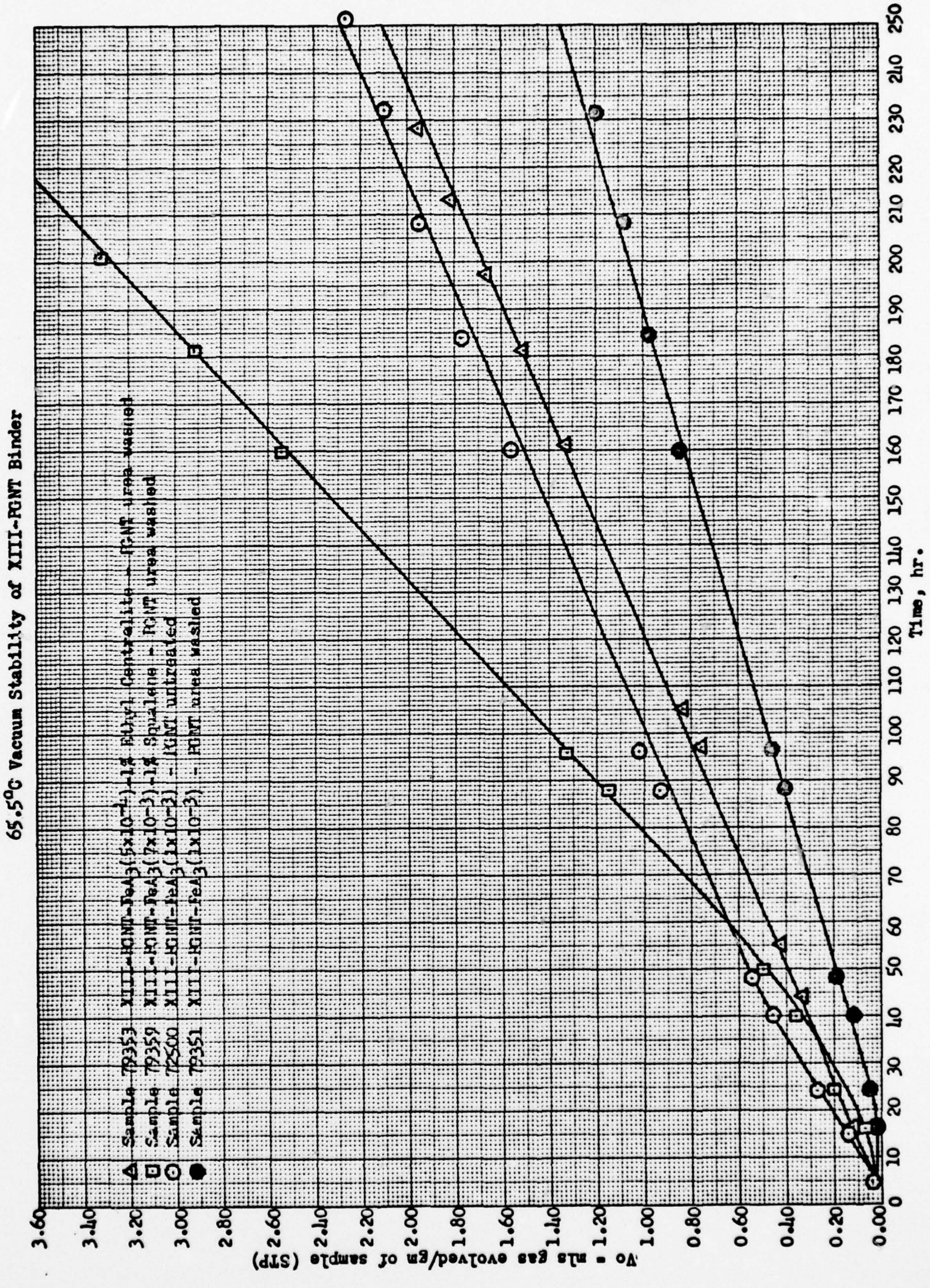

65.5°C Vacuum Stability of XIII-PGNT Binder

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Figure 7

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65.5°C Vacuum Stability XIII-PGNT-AP Castings

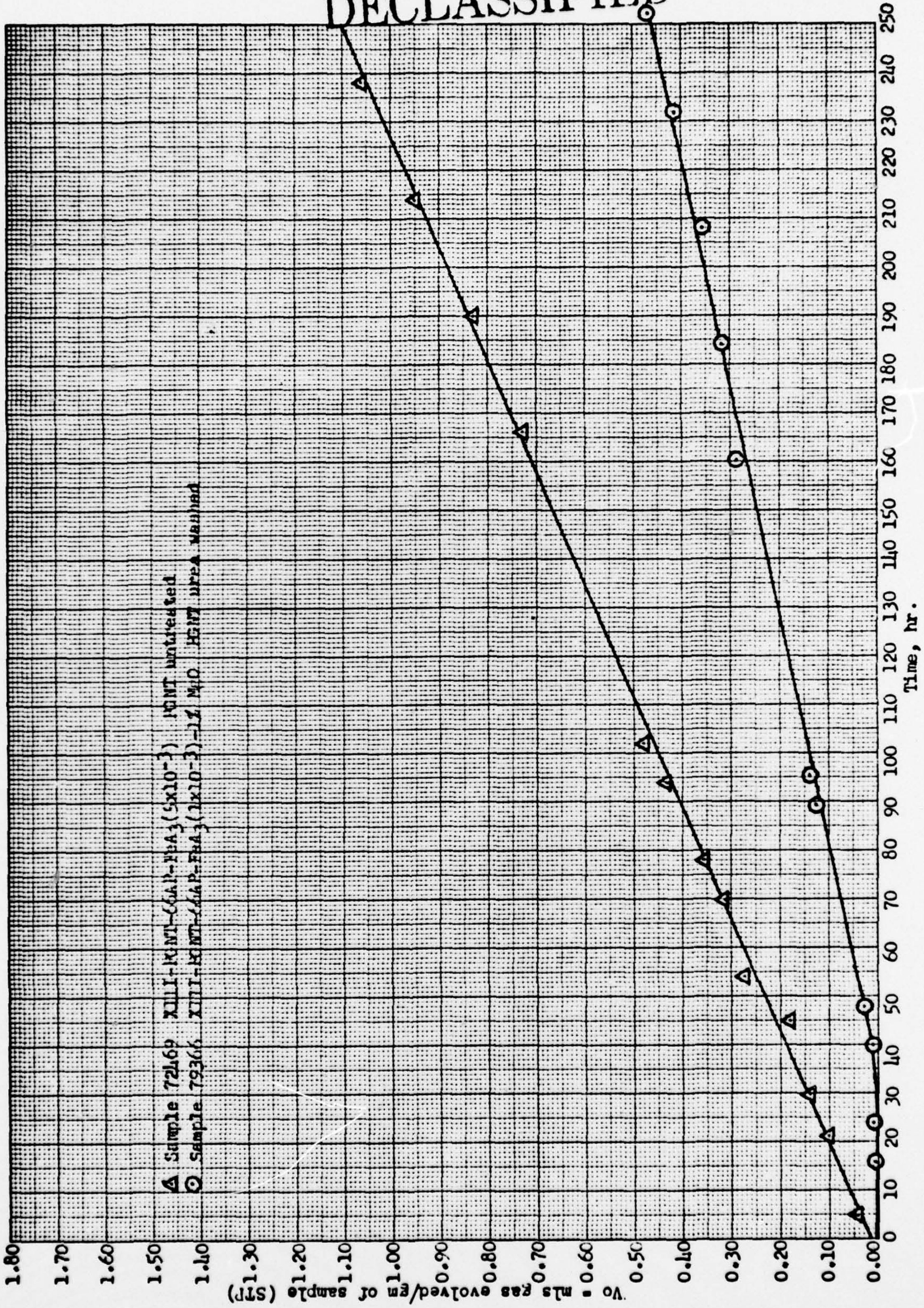

Figure 8

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82.5°C Vacuum Stability of XIII-PONT-66AP-$FeA_3(1x10^{-3})$-1% MgO

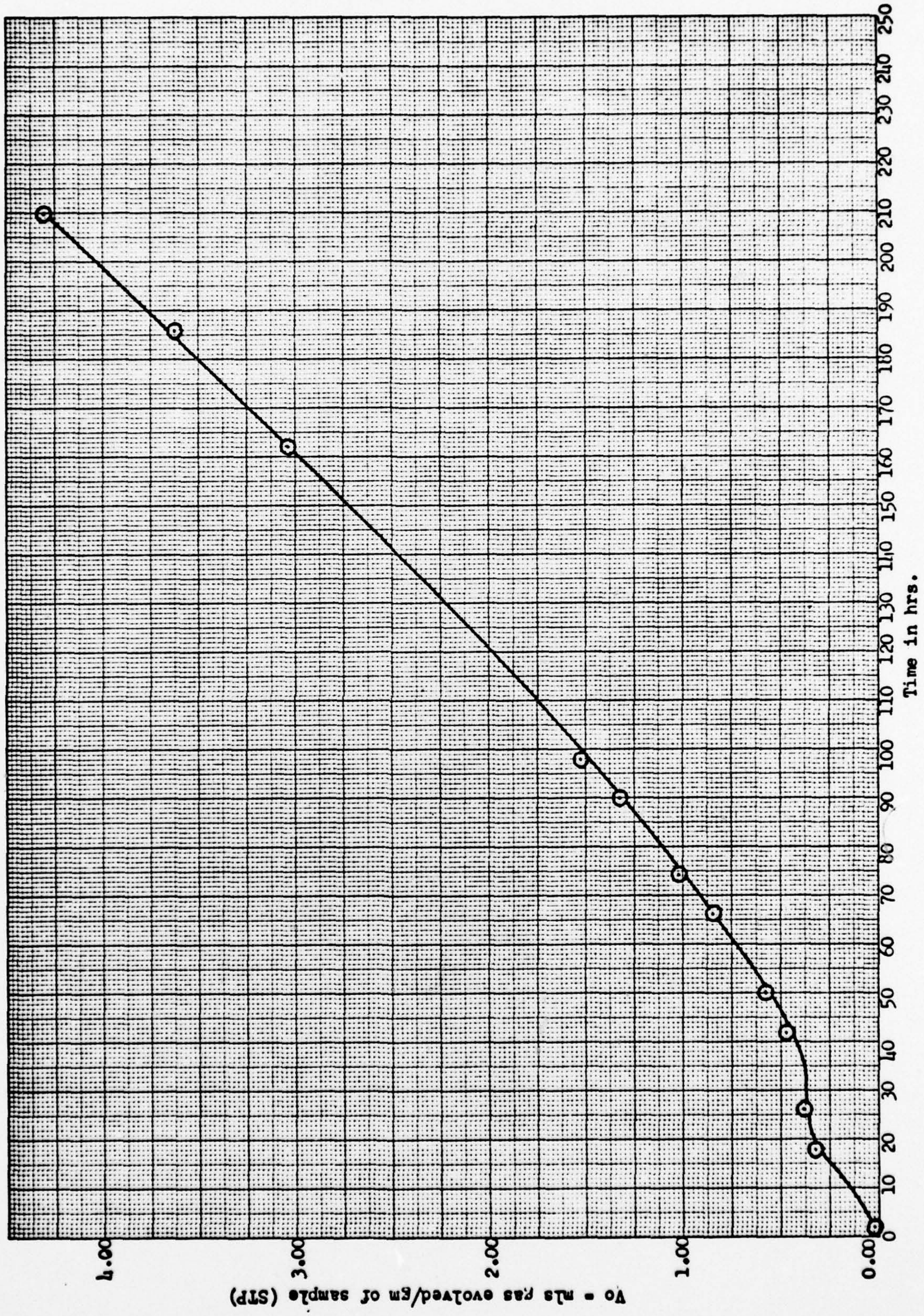

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Figure 9

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102	$Th(NO_3)_4 \cdot 4H_2O$ (thorium nitrate hydrate)
103	$SnCl_2 \cdot 2H_2O$ (stannous chloride hydrate)
104	$SnCl_2$ (stannous chloride)
105	$UO_2(NO_3)_2 \cdot 6H_2O$ (uranyl nitrate hydrate)
106	$Pb(OAc)_2 \cdot 3H_2O$ (lead acetate hydrate)
107	$Cu(NO_3)_2 \cdot 3H_2O$ (cupric nitrate hydrate)
108	FSO_3H (fluosulfonic acid)
109	$Co(NO_3)_2 \cdot 6H_2O$ (cobaltous nitrate hydrate)
110	$Ni(NO_3)_2 \cdot 6H_2O$ (nickel nitrate hydrate)
111	$Zn(NO_3)_2 \cdot 6H_2O$ (zinc nitrate hydrate)
112	$ZnBr_2$ (zinc bromide)
113	$Fe(SCN)_3$ (ferric thiocyanate)
114	$FeCl_3$ (ferric chloride)
115	CrO_3 (chromic oxide)
116	$K_3Cu(CN)_4$ (potassium copper cyanide)
117	$Hg(OAc)_2$ (mercuric acetate)
118	$Ce(NO_3)_3 \cdot 6H_2O$ (cerous nitrate hydrate)
119	$SnCl_4$ (stannic chloride)
120	$BiCl_3$ (bismuth trichloride)
121	$MoCl_5$ (molybdenum pentachloride)

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Code Number	Chemical
122	$Fe(ClO_4)_3 \cdot ?H_2O^*$ (ferric perchlorate hydrate)
123	$Fe(ClO_4)_2 \cdot ?H_2O^*$ (ferrous perchlorate hydrate)
124	1,10-phenanthroline ferrous perchlorate
125	$Cu(ClO_4)_2 \cdot 6H_2O$ (cupric perchlorate hydrate)
126	$Zn(ClO_4)_2 \cdot 6H_2O$ (zinc perchlorate hydrate)
127	$Pb(ClO_4)_2 \cdot 3H_2O$ (lead perchlorate hydrate)
128	$Co(ClO_4)_2 \cdot 6H_2O$ (cobaltous perchlorate hydrate)
129	$Ni(ClO_4)_2 \cdot 6H_2O$ (nickel perchlorate hydrate)
130	α,α'-dipyridyl ferrous perchlorate

---

*The hexahydrate was dried in vacuo over phosphorous pentoxide at 25°C. The weight loss corresponded roughly to the loss of 3 mol of water.

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