NASA CR-132357

# A STUDY OF THE EFFECTS OF SOLID PHASE REACTIONS ON THE THERMAL DEGRADATION AND BALLISTIC PROPERTIES OF SOLID PROPELLANTS

By Willfred G. Schmidt

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Prepared under Contract No. NAS1-11702 by
Aerojet Solid Propulsion Company
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## ABSTRACT

The thermal stability of perchlorate composite propellants has been studied at 135 and 170°C. Based on results obtained from previous studies on the thermal stability of $NH_4ClO_4$ composites, the experimental efforts of this program have been concentrated on determining the importance of heterogeneous oxidizer-fuel reactions in the thermal degradation process. The experimental approach used to elucidate the mechanisms by which the oxidizer fuel composites thermally degrade was divided into two parts, (1) keeping the fuel constant and varying the nature of the oxidizer and (2) holding the oxidizer constant and varying the fuel components. The fuel component primarily utilized in the first phase was polyethylene. Oxidizers included $KClO_4$, $KClO_3$, $NH_4ClO_4$ and $NH_4ClO_4$ doped with materials such as chlorate, phosphate and arsenate. In the second phase the oxidizer used was primarily $NH_4ClO_4$ while the fuels included saturated and unsaturated polybutadiene prepolymers and a series of bonding agents. Techniques employed in the current study include thermogravimetric measurements (TGA), differential thermal analysis (DTA, DSC), infrared (IR), mass spectrometry, electron microscopy and appropriate wet chemical analysis.

## SUMMARY

An investigation was conducted on the thermal degradation, i.e., aging, of a number of composite propellants. The tests included both model oxidizer-fuel composites and a production propellant. The model systems were studied at the relatively high temperatures of 170°C while the propellant was subjected to temperatures of 135°C for extended time periods (some in excess of 400 hours). The study concentrated on the thermal stability of the two primary constitutents, oxidizer and fuel, and the possible chemical interactions between these two components. The oxidizers studied were all perchlorate salts with the major emphasis on $NH_4ClO_4$ while the fuels investigated were essentially hydrocarbons, both saturated and unsaturated. While a detailed mechanism of the degradation of $NH_4ClO_4$-hydrocarbon composites is not yet fully understood a preliminary qualitative mechanism is outlined. An important conclusion from the present study is that the initial step in the overall degradation of the composite is the decomposition of the oxidizer. This conclusion is supported by the thermal behavior of composites using doped $NH_4ClO_4$ and by direct observations of propellant using both optical and electron microscopy. The former studies show that 'pure' $NH_4ClO_4$ is only moderately thermally stable. Catalytic impurities such as chlorate ion accelerate the degradation mechanism while negative catalytic anions such as arsenate and phosphate result in a significant increase in the thermal stability of $NH_4ClO_4$ composities. Microscopy indicates that decomposition is initiated by individual oxidizer particles. The number of oxidizer particles showing signs of decomposition after a given time-temperature history is a function of the nature of oxidizer, i.e., type and quantity of impurities. After initiation the decomposition of the composite propagates by reactions at the binder-oxidizer interface. Examination of failure sites, by electron microscopy, indicates that overall propellant failure occurs when the bonding degrades between a sufficient number (not yet defined) of oxidizer particles and the binder. The importance of the fuel in determining the thermal stability of a composite propellant is related to its role in these interface reactions. The oxidative degradation of the fuel (polymer) probably proceeds, or at least is initiated, by a radical attack. The experimental evidence suggests that the first step most likely involves a radical, from the oxidizer decomposition, abstracting a hydrogen atom from the hydrocarbon. In the present experiments there was little evidence, that once the initial hydrogen was abstracted, the polymer continued to degrade by a radical mechanism. Rather, the data indicate that the initially formed hydrocarbon radical either reacts with another oxidizing species forming some type of carbon-oxygen bond or with a second hydrocarbon radical forming a crosslink between chains.

## INTRODUCTION

This program is designed to study the effects of solid phase reactions on the thermal degradation and ballistic properties of solid propellants. The primary emphasis in the program is the investigation of those mechanisms by which the oxidizer, specifically ammonium perchlorate (AP), reacts with organic fuels at temperatures up to 200°C. The purpose of the study is to provide the information needed to successfully make composite propellants which can be heat sterilized or in other ways subjected to storage at elevated temperatures without altering those properties of the propellant which affect its ballistic performance.

All composite propellants are known to age, that is, some of their physical properties change with time. This aging may be due to a change in one of the constituents, e.g., plasticizer migration, the interaction of several components, e.g., oxidizer-fuel reaction, or the reaction of a component with the environment, e.g., surface air oxidation. The experimental efforts of the current program have been concentrated on the problem of the oxidizer-fuel reaction. All of these problems tend to be aggrevated at higher temperatures. They are therefore of particular concern to the NASA sterilizable motor program (Reference 1) where a composite propellant is subjected to temperatures as high as 135°C for extended time periods.

It has long been noted that when ammonium perchlorate is mixed with an organic fuel the composite undergoes thermal degradation in time periods which are significantly shorter than it takes the individual components to degrade at the same temperature. Clearly heterogeneous reactions at the interface between the components (fuel-oxidizer) are important when the components are in intimate contact at these temperatures. The current approach has been to identify and study the reactions leading to the thermal degradation of model and candidate composite propellants. Work under previous NASA contracts (References 2, 3 and 4) provides a starting point for an experimental approach to this problem.

As noted earlier, the thermal degradation of a composite propellant involves reactions which occur at the interface between the oxidizer and fuel components. Since these reactions involve only a small percentage of the total reactants one important experimental problem is the development of analytical techniques which are sensitive enough to detect changes at or below the one percent level. Techniques employed in the current study include thermogravimetric measurements (TGA), differential thermal analysis (DTA, DSC), infrared (IR), mass spectrometry, electron microscopy and appropriate wet chemical analysis.

The experimental approach used to elucidate the mechanisms by which the oxidizer fuel composites thermally degrade was divided into two parts, (1) keeping the fuel constant and varying the nature of the oxidizer and (2) holding the oxidizer constant and varying the fuel components. The

first part primarily utilized polyethylene as the fuel component. Oxidizers included $KClO_4$, $KClO_3$, $NH_4ClO_4$ and $NH_4ClO_4$ doped with materials such as chlorate, phosphate and arsenate. In the second phase the oxidizer was primarily $NH_4ClO_4$ while the fuels included saturated and unsaturated polybutadiene prepolymers and a series of bonding agents.

When necessary, materials were synthesized to meet the demands of the program. The experimental work utilized several different thermogravimetric balances, differential thermal and scanning calorimetric equipment. Analysis was performed using data obtained both with reflected and transmitted infrared (IR), mass spectrometry and appropriate wet chemical analytical techniques.

## I. EXPERIMENTAL

### A. EQUIPMENT

The basic instrument used in the infrared (IR) spectroscopic studies is the Beckman IR-9. An attenuated total reflectance (ATR) attachment is used for direct infrared analysis of the surface of solid samples. The attachment allows the angle of reflectance, from the crystal sample interface, to be varied from 30 to 60 degrees. Two different crystals, ZnS and KRS-5 (Thallous-bromide Iodide), are available as windows in the ATR attachment. Additionally, IR analysis are performed using KBr pellets containing the material to be analyzed.

All differential thermal analyses (DTA) are performed with a duPont 900 DTA. Non-isothermal thermogravimetric analyses are performed with an attachment to the duPont 900 (TGA 950). Isothermal decompositions are run on an Ainsworth automatic recording balance using a Honeywell temperature controller. Temperature control at 300°C is $\pm$2°C. The sample temperature is measured by a Pt-Pt. 10% Rh thermocouple located immediately below the sample holder.

Mass spectra are obtained with a CEC 103 spectrometer. The samples are handled on a high vacuum line and transferred to the mass spectrometer by breaking a glass seal in the sample tube.

### B. SAMPLES

#### 1. Oxidizer

##### a. Recrystallized $NH_4ClO_4$

All experiments in this program are performed using a single lot of ammonium perchlorate (AP). The AP has been recrystallized twice from an aqueous solution that is kept at a pH of $\sim$7-8 by the addition

of small amounts of $NH_4OH$. This AP is dried for 48 hours under vacuum at 50°C. It is used in all control experiments and serves as the starting material for any doped AP that is required. Before using oxidizers in laboratory tests or in propellants they are ground in a mortar and then screened to the desired particle sizes.

b. AP Containing Chlorate

The required amount of AP is dissolved in water at ∿60°C. The desired amount of $KClO_3$ is then added and the solution taken to dryness under vacuum at ∿50°C. $^3$Chlorate is analyzed for by the method of Chen (Reference 5). This is a spectrophotometric method in which ferrous ion is used as a reducing agent. The quantity of ferric ion produced is measured spectrally, in a sulfuric acid medium, at 300mμ.

c. AP Containing Phosphate

The following is the procedure used in the preparation of AP containing a small percentage of phosphate. In this report phosphate is taken to mean the sum of $H_2PO_4^-$, $HPO_4^=$, and $PO_4^{\equiv}$ since the exact form in the crystal is not known. Dissolve AP in water at ∿60°C (AP to $H_2O$ ∿ 1:2). Add $(NH_4)_2HPO_4$ and continue stirring until all salts are dissolved. The temperature is kept below 65°C. The solution is then cooled to ∿5°C in an ice bath and filtered. The crystals are dried in a vacuum oven at 50°C for 72 hours. Phosphate is analyzed for by the method of Gee and Deitz (Reference 6). It was experimentally determined that the AP did not affect this method of analysis. The method is a spectrophotometric one utilizing a mixed molybdate-metavanadate solution to develop the color. Measurements are made in the region of 350-400mμ. The analysis is sensitive to the acid concentration which must be reproducibly controlled.

d. AP Containing Arsenate

$As_2O_5$ is dissolved in water to form arsenic acid, $H_3AsO_4$. The pH of the solution is then adjusted with $NH_4OH$ such that the dominant arsenic containing species are $H_2AsO_4^-$ and $HAsO_4^=$. The procedure for making arsenic doped AP is essentially the same as that described for doping the AP with phosphate. Arsenic is analyzed for by first reducing it to arsine, $AsH_3$, with zinc in acid solution. The arsine is then passed into a pyridine solution of silver diethyldithiocarbamate. The arsenic reacts with the silver salt forming a soluble red complex which is measured photometrically at 530mμ (Reference 7). The percentage of arsenate reported is taken to be the sum of $H_2AsO_4^-$, $HAsO_4^=$ and $AsO_4^{\equiv}$ since the form of the anion in the crystal is not known.

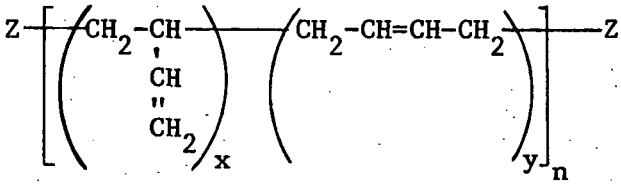
e. AP Containing Carbonate

The procedure is again essentially that used in doping the AP with phosphate. The carbonate is added in the form of ammonium bicarbonate. Again the species in the crystal is not known but will be considered a sum of $HCO_3^-$ and $CO_3^=$. As with the other oxidizer preparations, the final material is dried at 50°C, under vacuum, for a minimum of 72 hours. At present a satisfactory technique for analyzing the amount of carbonate in the AP has not yet been perfected.

2. Binder Ingredients

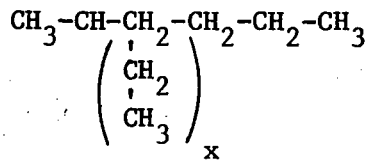
a. Prepolymer

Several unsaturated polybutadiene prepolymers with the following basic structure were used in the program



Z = COOH or OH

The two saturated prepolymers used were one from Phillips and one from General Tire and Rubber (Telagen). Since the latter is the prepolymer used in the NASA sterilizable motor program (Reference 1) the majority of experiments with saturated prepolymers used this material.



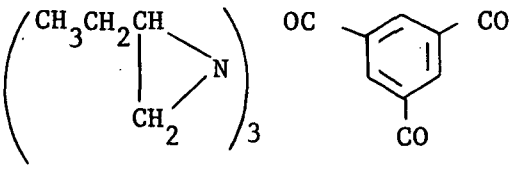
x ∿ 20 mole % of the total carbon is in the side chains.

This material was obtained from the sterilizable motor program where it had been stripped, i.e., two passes through a wipe film column at ∿200°C.

b. Cured Polymers

The unsaturated carboxy-terminated polybutadiene (U-CTPB) prepolymer was cured with the butylene imine derivative of trimesic acid (BITA).

BITA

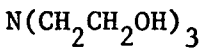


The proportion used was U-CTPB 95.93% and BITA 4.07% and the polymer cured at 60°C for 7 days.

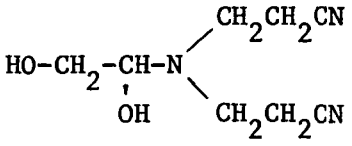
The polyethylene used in thermogravimetric experiments was obtained from U. S. Industrial Chemicals Company.

c. Bonding Agents

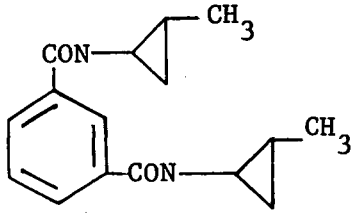
(1) Triethanolamine (Union Carbide)



(2) C-1 (American Cyanimide)



(3) HX-752 (3M)



## II. RESULTS

The primary obstacle to obtaining an understanding of the heat stability of a composite propellant is the fact that the extent of decomposition or reaction which must occur before the structural integrity of the propellant is impaired is very small. Therefore, the experimental

problem is to first determine this point of reaction or decomposition and second to devise and use experimental techniques which can follow these small chemical changes.

## A. INFRARED

### 1. Reflectance IR

Spectra obtained with reflectance IR are similar to those obtained with transmittance IR, however, they are generally not as sharp or as detailed. The intensity of the spectra depend primarily on the total sample surface area in contact with crystal window since the reflectance is from the sample-window interface. This contact depends to a large extent on the physical properties of the sample. For example, a 'soft' polymer will make good contact while a hard or brittle material may make contact with the crystal in only a few places. The type of crystal to be used and the angle of reflectance that would give the best possible spectrum had to be determined experimentally.

#### a. Ammonium Perchlorate

AP was compacted into thin pressed powder disks in a three quarter inch die at a pressure of 35,000 psi. A reflectance spectrum of AP, Figure 1, shows distinctive peaks at the following wave numbers, 625, $\sim$1100, 1400 and 3150 $cm^{-1}$. All four peaks have approximately the same intensity. The 625 $cm^{-1}$ and the 1400 $cm^{-1}$ peaks are relatively sharp while the peak at 3150 $cm^{-1}$ is broad. The absorption at $\sim$1100 $cm^{-1}$ is very broad and consists of three bands with individual peaks at 1085, 1100 and 1140 $cm^{-1}$.

#### b. U-CTPB - BITA Polymer

It was experimentally determined that the best reflectance spectrum was obtained with a KRS-5 crystal and an incident angle of 45°. The spectrum of this polymer has the following peaks, Figure 2.

| Wave Number ($cm^{-1}$) | Relative Intensity* |
|---|---|
| 690 | w |
| 740 | w |
| 910 | s |
| 965 | s |
| 995 | w |
| 1450 | m |
| 1650 | w |
| 2850 | w |
| 2920 | m |
| 3010 | w |

* w = weak; m = medium; s = strong

The strong absorptions at 910 and 965 $cm^{-1}$ are from the prepolymer unsaturation while the series of bands between 2850 and 3010 are due to various CH stretching and bending vibrations.

c. Polymer (UCTPB-BITA)-Oxidizer

A layer of AP was deposited on the surface of the U-CTPB polymer by evaporating an aqueous solution of AP from the polymer surface. Figure 3 shows that in reflectance IR the AP surface obscures the polymeric absorptions. The resultant is a broad smeared out spectrum of AP. The AP coated sample was heated at 175°C for two hours under a $N_2$ atmosphere. Figure 3 shows that the IR spectra of the material after heating has even poorer resolution than the spectra of the starting material. The AP was washed from the surface and the sample rerun, Figure 4. From this figure it can be seen that the IR spectrum is essentially that of the original polymer but at a reduced intensity (including the CH vibrations at $\sim$2900 $cm^{-1}$). The surface which had turned black was relatively brittle. This outer layer was pulled away from the bulk of the polymer and an IR of the subsurface, Figure 4, shows it to be the same as the polymer before heating.

The experiment was repeated using $HClO_4$, from a solution of $CH_3OH$, as the oxidizer. In the IR spectrum of this combination, before heating, both absorptions from the polymer, e.g. 925 $cm^{-1}$, and perchlorate, e.g. 1100 $cm^{-1}$, can be noted, Figure 5. Heating the sample for 2 hours at 175°C under $N_2$ again produced a black hard surface on the polymer. An IR spectrum of the surface, Figure 5, shows the characteristic polymer absorptions but at a reduced intensity. The perchlorate band at 1100 $cm^{-1}$ appears to have decreased to a greater extent than the polymer absorptions.

2. IR Using KBr Pellets

The relatively poor spectra obtained with reflectance IR led to a change in emphasis from surface reactions to bulk decomposition with the residues being analyzed by transmittance IR (KBr pellets).

The polymer selected for the initial work was polyethylene (PE). PE was selected as a model for the saturated backbone polymer system used in the heat sterilization program. PE has the advantage of not having functional groups thereby limiting the initial decomposition to a reaction between the oxidizer and the saturated hydrocarbon. The PE used melts at $\sim$110°C and therefore assures good surface contact with the oxidizer for heterogeneous decomposition reactions.

The oxidizers investigated were: (1) recrystallized AP, (2) AP cocrystallized with 0.025% chlorate (percentage based on analysis), (3) $KClO_4$, (4) $KClO_3$, and (5) AP (JPL Lot #310) (Reference 8). For these experiments the oxidizer-fuel ratio was arbitrarily selected as 75/25 (weight percent). The oxidizer particle size in all the reported experiments was kept constant at $\overline{75\mu}$ (62-88$\mu$).

The IR spectra of PE (KBr pellet) is shown in Figure 6. The primary absorptions, which are all related to the C-H group, are at the following wave numbers ($cm^{-1}$).

720
1470
2850
2940

It was previously shown that the primary absorption due to AP are at 625, 1100, 1400 and 3150 $cm^{-1}$. Figures 7, 8 and 9 are spectra of PE mixed with AP, $KClO_4$ and $KClO_3$, respectively. It can be noted that the absorptions due to the PE are relatively weaker than those of the oxidizer even after allowing for the 3 to 1 (oxidizer/PE) weight ratio. The potassium salts do not have the absorptions at 1400 and 3150 that are due to the ammonium ion in the AP spectra. The most notable difference between the $ClO_4^-$ ion and the $ClO_3^-$ ion is that the broad triple peak at $\sim$1100 $cm^{-1}$ ($ClO_4^-$) becomes a single peak at $\sim$980 $cm^{-1}$ ($ClO_3^-$). This shift is sufficient to distinguish $ClO_3^-$ ion in the presence of $ClO_4^-$ ion. However, in the chlorate-doped AP sample the chlorate concentration is so low that this absorption is not detectable.

The AP-PE samples were heated, in the TGA at 170°C, until $\sim$1% weight loss was recorded. After removing the 100 mg samples from the TGA, it was noted that the samples had turned black when the oxidizer was $NH_4ClO_4$ and brown when the oxidizer was $KClO_4$ or $KClO_3$. This color change was already significant at a time when the overall weight loss was $\leq$1%. This residue (oxidizer-recrystallized AP), was ground and made into a KBr pellet, Figure 10. It can be seen that the AP still dominates the IR spectrum.

To overcome the above problem the residues were boiled in water for 15 to 30 minutes. The solution was filtered hot and the residue dried at 75°C for 24 hours. These washed and dried residues were then made into KBr pellets. Figures 11 and 12 are examples of the results of this analysis. In all of these figures it can be seen that some perchlorate or chlorate remained in the residue (i.e., peaks at $\sim$720 and $\sim$1100 for perchlorate and 720 and 980 for chlorate). The weaker ammonium absorption at $\sim$3150 is essentially gone in the IR of the residue. The inability to remove all of the inorganic oxidizer is due to the fact that the physical properties of the PE were altered. Most notably the residual

material no longer melted at any temperature up to 300°C. As the original melted PE solidified it coated some AP in such a way that the two materials could no longer be separated.

The part of the spectra that is of particular interest in these studies is the appearance of bands near 1200 $cm^{-1}$ and between 1740 and 1770 $cm^{-1}$. Absorptions near 1200 $cm^{-1}$ are most likely due to C-O groups while those in the region of 1700 $cm^{-1}$ are due primarily to C=O (ketone or carboxylic acid). It was not possible to establish the presence of C-Cl bonds ($\sim$600-800 $cm^{-1}$). It is interesting to note that the formation of carbon-oxygen bonds occurred in all four samples.

B. THERMOGRAVIMETRIC DATA

1. Polyethylene - Variable Oxidizers

a. Potassium and Ammonium Salts

Potassium and ammonium oxidizing salts were mixed with PE to determine the effect of the ammonium ion. Unlike the potassium, the ammonium ion can be oxidized or it can provide a proton with which to form an acid e.g. perchloric acid. The primary difference noted appears to be that the decomposition with the potassium salts is essentially decelaratory in nature while the ammonium oxidizers start decomposing slowly but accelerate with time, Figures 13 and 14. The accelerated decomposition of the recrystallized AP is not seen in Figure 13 because the total time of the experiment is too short. Other data have shown that the decomposition of the recrystallized AP composite eventually becomes acceleratory. However, the rate does not become as great as that of the chlorate doped material. All the experiments described were with 100 mg samples of the PE/oxidizer mixture heated in a nitrogen atmosphere at 170°C.

b. Doped $NH_4ClO_4$

The oxidizers investigated were: (1) recrystallized AP, (2) AP cocrystallized with 0.025% chlorate (percentages based on analysis), (3) AP doped with 0.19% $H_2AsO_4$, (4) AP doped with 0.08% $H_2PO_4$ and (5) AP cocrystallized with ammonium bicarbonate. For these experiments the oxidizer-fuel ratio was selected as 75/25 (weight percent) and the oxidizer particle size was kept constant at 75μ (62-88μ).

Since the polyethylene melts at a temperature ($\sim$110°C) which is below the final reaction temperature (170°C) unscreened PE was used in these experiments. This proved to be a mistake. The results with the control (pure AP) formulation did not agree with the previous TGA data which was obtained using 62-105μ PE. On examining the composites on a hot stage

microscope it was seen that while the large particles of PE melted, the melt did not spread out uniformly. This resulted in some of the AP not being in contact with the melted PE. The TGA data obtained, using the larger particle PE, are internally consistent but can be compared to previous results only qualitatively.

(1) DTA of Doped AP

The AP was doped as described in the experimental section. DTA's were run on the dried oxidizer and are shown in Figures 15 and 16. It can be seen that the onset of the exotherm associated with the low temperature decomposition is affected by the nature of the dopant. However, the effect is relatively small, i.e., the onset for the control AP was ∿310°C and for the carbonate doped material ∿307°C. The addition of arsenate shifted the onset of the AP low temperature exotherm to ∿328°C and to ∿324°C for the phosphate doped material.

(2) Temperature Programmed TGA

∿10 mg samples of these blends were placed in the duPont 950 TGA. The experiment was started at room temperature (slow $N_2$ flow) using a heating rate of 10°C/min. The results were replotted and are shown in Figure 17. Above 250°C weight loss becomes significant with the rate accelerating rapidly. The pure AP sample deflagrated at 395°C after a weight loss of ∿22% while the carbonate doped AP deflagrated at 395°C after a weight loss of ∿26%. With the arsenate doped sample the rate of weight loss was approximately the same as the previous two samples; however, decomposition continues smoothly until all the AP is consumed at ∿435°C. The phosphate doped sample shows the greatest change in that decomposition did not begin until ∿300°C, after which it decomposed slowly until ∿450°C where the remining (∿78%) sample deflagrated.

(3) Isothermal TGA

The four mixtures were heated, using the Ainsworth thermogravimetric balance, in a nitrogen atmosphere at 170°C. The emphasis in these experiments was on the length of the induction time, $\gamma$, and the early stages of decomposition, e.g., up to ∿3% weight loss. Figure 18 is a plot of these data. From an examination of the induction time, time to first detectable weight loss, it can be seen that the samples fall into two groups. The pure AP and the carbonate doped AP have an induction time of ∿4 hours while the $\gamma$ for arsenate and phosphate doped AP is ∿15 hours. An examination of the rate of decomposition after the induction period shows that the above division is still valid. That is, once the pure AP and the carbonate doped AP start decomposing the rate is linear up to ∿2% after which it accelerates. With the arsenate and phosphate doped AP the initial rate of decomposition, ∿0.025%/hour, is significantly lower than that of the pure AP (0.056%/hour) or the carbonate doped AP (0.050%/hour). The difference between the arsenate and phosphate doped AP mixtures is the point at which the decomposition begins to accelerate. For the arsenate this is at ∿0.3% decomposition (i.e., 36 hours) while for the phosphate it occurred at ∿1.7% (i.e., 90 hours). It is interesting to note that after the point is reached where the decomposition rate begins to accelerate all four samples decompose at approximately the same rate.

## 2. Saturated and Unsaturated Prepolymers

In these experiments larger samples, 500 mg, were used in an attempt to more accurately examine the early stages of decomposition. A 50/50 mixture of the AP and polymer was used with the AP particle size held constant at 75μ (62-88μ). All experiments were performed at 175°C under a nitrogen atmosphere. Three oxidizers, recrystallized AP, phosphate doped (0.08%) AP and chlorate doped (0.025%) AP, were mixed with each prepolymer. In addition some of the recrystallized AP was coated with different bonding agents. The coating procedure involved dissolving the coating agent in dry dioxane. To this was added the AP and the slurry was stirred at room temperature for 48 hours. The coated AP was filtered and then dried at room temperature under partial vacuum. The resultant oxidizer was mixed with the prepolymer and the mixtures decomposed in the thermogravimetric apparatus.

### a. Unsaturated Prepolymer

Figure 19 shows that the initial rate of weight loss, up to ∿0.2%, is about the same for all three oxidizers. After that the chlorate doped material accelerates rapidly while the phosphate doped and control AP sample tend to level off. The decomposition rates with these materials remained relatively the same until >50 hours at which time the control AP sample started to accelerate slightly.

When the effect of the three bonding agents is examined it can be seen, Figure 20, that the one, triethanolamine, which reacts with the AP to form a salt on the surface caused the fastest rate of decomposition of the mixture. The mixtures with the bonding agent adsorbed to the AP (C-1) and that polymerized on the AP (HX-752) had approximately the same rate of decomposition.

### b. Saturated Prepolymer

The overall results compare with those of the unsaturated binder. That is, the chlorate doped oxidizer has the greatest rate of decomposition of the various oxidizers, Figure 21, and the TEA coated AP resulted in the fastest decomposition among the bonding agents, Figure 22.

In general the rate of weight loss, for comparable samples, was greater with the saturated than the unsaturated binder. In all cases the samples were discolored to dark brown or black at 1% weight loss and both prepolymers showed an increase in crosslinking at this point. Control runs of the two prepolymers, Figure 23, showed the same difference in rate of weight loss (unsaturated was faster), very little discoloration and only a slight increase in hardening. The residues of the oxidizer-prepolymer samples were not brittle enought to grind for IR (KBr pellets) so an attempt at analysis

was made using reflectance IR. The method being relatively insensitive to small, <5%, changes showed very little of interest on the regular scan. However, when the sensitivity was increased and the region between 1500 and 1800 $cm^{-1}$ scanned some sharp peaks associated with carbon-oxygen and amide bonds appeared, Figure 24. With the unsaturated prepolymer there are two regions of absorption, 1640 and 1720-1740 $cm^{-1}$ while with the saturated prepolymer there is one dominant absorption at 1720 $cm^{-1}$.

C. MASS SPECTROMETRY

The two samples analyzed by mass spectrometry were composites containing pure AP and chlorate-doped AP as oxidizer and PE as the fuel. In each case 50 mg of the sample was placed in a U-shaped tube containing a glass break seal. After evacuating the system down to <5μ it was closed off from the pump. The sample temperature was raised to ∿120°C and left until there was no further increase in pressure (∿15 minutes). This procedure eliminated adsorbed $H_2O$, etc. The sample tube was again pumped down to <5μ and sealed off with a torch.

The sealed tube was then placed in an oven at 170°C. The sample containing pure AP was left for 45 hours while that containing chlorate doped AP was left for 8 hours. The tubes were then placed on the mass spectrometer vacuum system and an enclosed magnetic bar dropped to break the seal. The major species found are listed below normalized to the 32 peak. The 32 peak, $O_2$, was chosen as the other major products do not have significant fragmentation species of mass 32. However, possible species such as $CH_3OH$ would be found at this mass number.

Table 1

MASS SPECTROMETER ANALYSIS

| Mass | Recrystallized AP | Chlorate Doped AP | Parent Compounds | Fragmentation Products from: |
|---|---|---|---|---|
| 12 | 0.08 | 0.08 | | $CO; CO_2$ |
| 14 | 0.33 | 0.35 | | $N_2$; $N_2O$; NO; $CH_4$ |
| 16 | 0.47 | 0.49 | $CH_4$ | $O_2$; $N_2O$; CO; $CO_2$ |
| 17 | 1.09 | 1.30 | $NH_3$ | $H_2O$ |
| 18 | 3.73 | 4.45 | $H_2O$ | |
| 28 | 1.28 | 1.50 | $N_2$; CO | $N_2O$; $CO_2$ |
| 30 | 0.85 | 0.84 | NO | $N_2O$ |
| 32 | 1.00 | 1.00 | $O_2$ | |
| 44 | 2.04 | 2.06 | $N_2O$; $CO_2$ | |

In addition to what was found, it is interesting to note the species that were not found. No species were recorded at 35 (Cl), 36 (HCl), or 70 ($Cl_2$) and very little at 100 ($HClO_4$).

The absence of chlorine containing species was disturbing and the possibility existed that these polar molecules were too strongly adsorbed to the glass to be detected. Therefore, a larger scale decomposition reaction was initiated using chlorate doped AP. A ∿3.2 gram sample of the mixture, AP (75%) PE (25%), was placed in a ceramic container and inserted into a horizontal tube furnace at 170°C. A slow nitrogen flow was kept moving through the tube during the period of heating. The nitrogen and product gases were bubbled through a solution of base (NaOH) at the exit of the furnace tube. The heating was continued for 48 hours. It was found that 8.94% of the original mixture had decomposed to gaseous products. An attempt to extract the residual AP from the PE with water was only partially successful. Attempts to extract the PE from the residue, with organic solvents, were unsuccessful. A DTA of the residue, run after these extractions, shows that the resolidified PE has occluded some AP. Further work with the residue showed that it no longer melted at any temperatures up to 400°C. Above 300°C decomposition began, most likely due to the occluded AP.

An analysis of the exit trap showed no trace of chlorate ion, 0.98m moles of $H^+$ and 1.45 moles of $Cl^-$. No $Cl^-$ was found in the water extracts of the residue. Because of the inability to separate the fuel and the oxidizer in the residue it was not possible to determine the fraction of each component decomposed. From the weight of the residue minus the weight loss determined by a TGA of the residue (thought to be primarily AP) it was estimated that ∿1.75m moles of AP decomposed during the reaction.

## D. ELECTRON MICROSCOPY

This technique was utilized relatively late in the program. A block of propellant (73-30-70)[1] which had been cycled 8 times on the Sterilizable Motor Program (Reference 1), and had failed between the 6th and 8th cycle, was cut apart after the 8th cycle. Several interesting observations were made when the fractured area was looked at under a microscope. One observation concerned the condition of the individual AP particles. It was noted that while some AP particles showed no signs of decomposition others were partially or almost entirely decomposed. This was the case even with particles that were adjacent to each other in the matrix. An additional observation was that if the AP particle showed signs of decomposition the bonds to the polymeric matric were broken. In some cases there was only a small decomposing oxidizer crystal left in a

(1) Telagen/Glycerol triricinoleate/isophorane diisocyanate/FC 217 (proprietary) bonding agent.

crater-like hole. These can be dramatically seen in Figure 25. How much of the crater was due to the AP decomposition and how much to polymer decomposition is not known. In several interesting cases AP particles were found which showed signs of decomposition on a part of the crystal only. In these cases the bonding between oxidizer and binder appeared to be relatively intact.

Several samples were cut from places in the propellant block which had not shown any signs of failure. At low magnification (x200) the overall surface looks porous compared to the control and there are definite signs of bonding failure between the AP and binder, Figure 26. Many of the larger AP particles are cracked. Since these samples were obtained by cutting the propellant, it is possible that the cracking occurs on sampling. It has been noted that significantly more AP crystals are fractured in cut samples which have been heat sterilized than in the controls. If the heated AP crystals do not crack in situ they may become more fragile and therefore fracture more easily on cutting.

A second propellant block (73-05-121)[2] which did not fail until the 6th and 8th cycle was sampled at the edge (the block was not cut to expose the failure area). The area between the larger AP crystals again looks porous. When this is further enlarged (x2000) the smaller AP particles can be seen to show signs of decomposition, Figure 27. The spherical aluminum particles ($\sim$5-10$\mu$) can be seen to be embedded in the polymeric matric while many of the AP crystals (15-40$\mu$) show signs of discontinuity at their boundaries with the polymer.

A third propellant (73-30-82)[3] which failed after two cycles is shown in Figure 28. The samples are again cut from the block. Even at x1000 the surface of the control shows good integrity between the polymer matrix and both the aluminum and AP particles. The heat cycled samples show signs of porosity, e.g. note the area surrounding the large AP crystal at x500. Finally a fourth sample (72-30-75)[4] which failed by two heat cycles shows a significant amount of porosity and cracking throughout the polymer matrix. In this case it appears as if the whole matrix has become disrupted so that even the aluminum particles are loosely held, Figure 29.

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(2) Similar to (1) except additional stabilizer added.
(3) Telagen/Trimethylolpropane/Dimer acid diisocyanate.
(4) Similar to (3) except has FC 154 (proprietary) bonding agent added.

## III. DISCUSSION

To improve the thermal stability of composite propellants two important questions must be answered:

(1) Where does decomposition begin?

(2) How does it propagate?

The experimental data appear to answer the first question quite conclusively but only suggest possible answers to the second.

The overriding factor in the determination of the stability of a composite is the nature of the oxidizer. This does just not mean gross changes in the nature of the oxidizer but small changes in the purity of a given oxidizer can have large effects on the thermal stability of the composite propellant. It has been well established that certain impurities in AP, such as $ClO_3^-$, accelerate the thermal decomposition of the AP and of composites containing this AP. Additionally, it has been shown that certain dopants, such as phosphate, act as negative catalysts in the thermal decomposition of AP (References 3 and 4).

A grey area has been the thermal stability of 'pure' AP. Here it has been found that the thermal stability of different lots of AP are not the same. Those lots which were found to be thermally less stable were analyzed for impurities such as $ClO_3^-$ to account for the reduced AP thermal stability. Inherent in this approach is the assumption that the more thermally stable the material, the 'purer' the AP. However, AP that has been formed from the neutralization of $HClO_4$ with $NH_3$ in pure water has been shown not to be particularly thermally stable (Reference 9). It is therefore postulated that the more thermally stable lots of AP may not be 'purer' but rather contain impurities which act as negative catalysts for the AP decomposition.

An earlier study (Reference 10) which analyzed many lots of AP, found some of the more stable lots to contain small amounts of a species that yielded CO and $CO_2$ in mass spectrometer analysis. It was suggested that these lots of AP contain small amounts of a carbonate impurity. In the current program ammonium bicarbonate, $NH_4HCO_3$, was added to the solution ($\sim$1% level) from which AP was recrystallized. The resultant material was not analyzed to determine the amount of carbonate incorporated into the AP. However, decomposition studies using this AP in mixtures with polyethylene have shown the AP to behave essentially the same as the control 'pure' AP. The lack of an adequate analytic procedure for determining the carbonate concentration in the doped AP crystal makes it difficult to interpret the results of experiments based on this oxidizer. The similarity of results with the carbonate doped AP and the control AP suggest that the carbonate was either not incorporated into the $NH_4ClO_4$ crystal or was later destroyed by the drying procedure. Ammonium bicarbonate is relatively unstable under the conditions used for drying, i.e. 50°C and vacuum.

When the dopant used is arsenate or phosphate there is a definite increase in the thermal stability of the AP composite. The relative effectiveness of these additives is not completely clear from the present study. In all respects but one, the induction time, the thermal stability of the phosphate doped AP is greater than that of the arsenate doped AP. However, the initiation of the low temperature exotherm as seen in DTA, Figure 16, or the end of the induction time as measured by isothermal TGA, Figure 18, show the two materials to be approximately equal.

Since it is in the early stages, prior to any significant weight loss, that the propellant fails both of these dopants may be equally effective in stabilizing the AP composite. All other considerations such as quantity of dopant (0.08 for phosphate vs 0.19 for arsenate) and decomposition rate after the induction time indicate that the phosphate is the more effective dopant. In any case, either of these anions could be found in the mother liquor from which AP is commercially crystallized. In the absence of positive catalysts such as chlorate ion it may be that these negative catalysts are important in determining the relative stabilities of different lots of AP.

An examination of a large number of AP particles that have been heated shows, that at a given time, some crystals are partially decomposed while others do not show any signs of decomposition. Therefore, while the overall rate of decomposition may be reproducible it is based on a statistical distribution among the individual particles. The current examination of the heat cycled motors has shown a similar effect even though the AP is in a polymeric matrix. That is, the decomposition begins with specific AP particles and the reaction then propagates by interface reaction between the binder and the initial AP decomposition products. A similar phenomena, decomposition originating at relatively few AP particles, has been noted in studies at JPL (Reference 11).

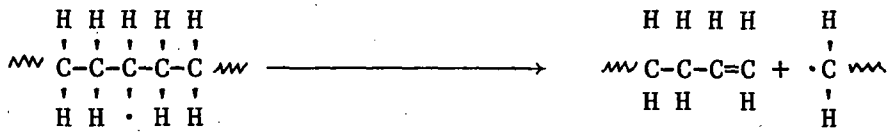
There is thus a strong indication that the initial step in the propellant degradation is a function of the oxidizer. If in fact it were some heterogeneous AP polymer reaction it could be expected that the effect would be general at all the oxidizer-polymer interfaces. If the initiation of the decomposition is a function only of the oxidizer it must occur even when there is no organic fuel present. Since under similar time-temperature conditions the AP is considered to be stable (weight loss or pressure measurements) the binder in some way must be responsible for propagating the reaction. This could be explained if, on the surface of the AP, the initial dissociation products are in equilibrium with the $NH_4ClO_4$ and the binder functions by reacting with these products and driving the dissociation forward.

It is this latter reaction that is not yet fully understood. The polymer could react directly with the primary dissociation product, $HClO_4$, or with a subsequent $HClO_4$ decomposition product e.g. such as could be formed in a bimolecular $HClO_4$ reaction.

The fact that the potassium salts oxidized the polyethylene indicates that the proton (or more specifically $HClO_4$) is not a necessary intermediate species. These data indicate that the polymer oxidation is initiated by a radical attack. However, at these temperatures the pure oxidizer does not decompose to a significant extent into radicals. The formation of radicals, such as O, OH, and $ClO_3$, through the breaking Cl-O or Cl-OH bonds requires considerable energy. If, however, once formed the radical can further react with the organic component the net reaction will be less endothermic or can even become exothermic thereby making this mode of decomposition possible at the relatively low temperatures (170°C) used in this study.

Since there is no reasonable path for direct acid attack on a saturated hydrocarbon like PE it is probable that even when the oxidizer is AP the initial oxidation of the polymer proceeds by a radical mechanism. The radicals being generated, for example, by the bimolecular reaction of $HClO_4$ on the AP surface. The strong effect, on decomposition, of $ClO_3$ as a dopout in $NH_4ClO_4$ is most likely related to its ability to increase the rate of production of radicals (the reactive $HClO_3$ could directly oxidize $NH_3$ or react rapidly with $HClO_4$). From the mass spectral analysis it is clear that the $NH_4ClO_4$ primarily breaks down in condensed phase reactions as there is no significant amount of unreacted $HClO_4$ of $NH_3$ produced. The experimentally determined 18/17 mass ratio in the instrument used in these analysis is 100/29.6. When this is applied to the data in Table 1, the 17 peak due to water fragmentation should be 1.10 (found 1.09) for the pure AP and 1.32 (found 1.30) for the chlorate-doped AP. This indicates very little free $NH_3$ was produced in the decomposition.

If a species such as $ClO_2$ is produced at these temperatures it would react very rapidly with any compound that could be oxidized. Therefore, the rate of the oxidation reaction would depend on the rate of the formation of the oxidizing radicals. The initial step in the reaction of a radical with polyethylene would most probably be the abstraction of a hydrogen atom. Once a hydrogen is abstracted from the PE there are several paths which the polymer can follow; (1) it can degrade by a radical process,



(2) it can react with further oxidizing species or (3) react with another polymer radical forming a crosslink between two polymer chains. The first path is not considered as a probable degradation mechanism (Reference 12) and this is supported by the lack of a significant number of hydrocarbon fragments in the gas phase and the lack of spectral evidence for double bonds.

The spectral evidence for carbon oxygen bond formation indicates that the second reaction does occur. However, the small amount of reactants involved and the relative insensitivity of the IR spectral method at these levels makes it impossible to tell quantitatively the extent of this reaction. Similarly, the extent of carbon-chlorine bond formation can only be approximated. In the IR region the carbon-chlorine bond is relatively weak and was not found in the current experiments. The best estimate is from the bulk decomposition experiment. It was difficult to determine the theoretical amount of chlorine as the decomposition residue could not be effectively separated into AP and fuel components. However, the best estimate, based on the weight of polymeric residue and the amount of AP in that residue (TGA data), showed that $\sim$1.75m mole of AP decomposed and $\sim$1.45m mole of $Cl^-$ was found in the trap. Therefore, based on the 1.75m mole estimate, at least 80-85% of the chlorine formed during decomposition came off as volatile species (most probably HCl) which could be trapped in a basic aqueous solution.

The last reaction path suggested, the reaction of two polymer radicals to form a crosslink appears to occur to a significant extent. In the bulk decomposition experiments it was found the PE is transformed from a low melting polymer to a material which does not melt at any temperature attained in the experiments (>400°C). The material is also essentially insoluble, a fact which made the titration for double bonds impossible. Changes in both the melting and solubility characteristics indicate that a considerable amount of crosslinking took place.

The experiments with the saturated and unsaturated hydrocarbon prepolymer basically substantiated the results obtained with the polyethylene. That is, the nature of the oxidizer is the primary factor determining the thermal stability of the composite. The current experiments were not successful in differentiating various prepolymer structures as to their ability to propagate the reaction initiated on the oxidizer surface. The results of the TGA experiments indicate that the unsaturated prepolymer is more resistant to reaction than the saturated hydrocarbon. However, it is known from experience gained on the Sterilizable Motor Program (Reference 1) that this is not the case. Several explanations are possible. One is that the products of decomposition add more readily to the unsaturated, especially at the allylic carbon, than to the saturated prepolymer. A second possibility is that at the temperature, 170-175°C, used to accelerate these experiments the controlling reactions are not the same as at 135°C which is the sterilization temperature.

More basically the problem may be that the experiments are measuring the wrong parameters. Structural damage does not require that the reaction leading to such damage produce volatile products (References 1 and 10). As noted earlier once the AP crystal starts to decompose the reaction continues at the AP-binder interface. It may well be that failure results when the bonding between a number of AP particles and the binder matrix breaks down. At what point failure occurs, i.e., how many binder-oxidizer interfaces must degrade, is undoubtedly a function of the stress on the propellant at that point and possibly dependent on factors such as the AP particle size distribution.

In order to further investigate these interface reactions recrystallized AP was coated with several materials which have been used as bonding agents. Triethanolamine (TEA) which reacts with the AP to form a salt at the AP surface, resulted in a significant decrease in thermal stability regardless of the binder system. The other two materials, one a substituted tertiary amine (C-1) which adsorbs to the AP surface and the second an aziridine (HX-752) which polymerizes on the AP, did not seem to affect, positively or negatively, the thermal stability to the AP-prepolymer mixture. While the aziridine was somewhat more stable the differences were small and again weight loss may be the wrong parameter to monitor to determine the stability which is important to high temperature composite aging. Changes which result in strong negative results, such as those with TEA, undoubtedly would lead to a less thermally stable propellant. The difficulty lies in differentiating between materials which appear to have relatively small effects such as the C-1 or HX-752.

## IV. CONCLUSIONS

While the detailed mechanism of the degradation of AP/fuel composites is not yet fully understood a qualitative picture has begun to emerge. The overall thermal stability of a composite propellant is a function of all of its ingredients. However, the primary component, at least in AP composites, which determines the thermal stability of the propellant is the oxidizer. Listed below are some of the important observations which must be incorporated into the final mechanism.

A. The initial step in the overall degradation of the composite is the decomposition of the oxidizer. Relevant to this conclusion are the following observations when the oxidizer is $NH_4ClO_4$.

1. Catalytic impurities such as $ClO_3^-$ accelerate the degradation mechanism.

2. Pure AP is only moderately thermally stable when mixed with a fuel component.

3. Negative catalytic anions such as arsenate and phosphate result in a significant increase in the thermal stability of AP composites.

B. After initiation, on the oxidizer surface, the decomposition propagates by reactions at the binder-oxidizer interface. Examination of failure sites indicates that overall propellant failure occurs when the bonding degrades between a sufficient number (not yet defined) of individual oxidizer particles and the binder. Related to the role of these interface reactions is the importance of any constituent of the composite which could be expected to be selectively adsorbed or bonded to the oxidizer surface.

C. The oxidation of the polymer most probably proceeds, or at least is initiated, by a radical attack. The experimental evidence suggests that the first step most likely involves a radical, from the oxidizer decomposition, abstracting a hydrogen atom from the hydrocarbon. There was little evidence, that once the initial hydrogen was abstracted, the polymer continued to degrade by a radical mechanism. Rather, the data indicate that the initially formed hydrocarbon radical either reacts with another oxidizing species forming some type of carbon-oxygen bond or with a second hydrocarbon radical forming a crosslink between chains.

Weight loss data are useful in determining relative thermal stabilities within a given system but are not particularly useful in comparing different systems. DTA and TGA are useful in providing a screening test for ingredients. Negative results from these tests, e.g., a short induction time or a rapid weight loss, are a good indication that the component or composite cannot be used in a thermally stable propellant. However, the converse, using positive results, is not necessarily valid as a predictive tool.

The most promising approach, to further research in this area, is the direct observation of the oxidizer-fuel interface region. An experimental approach to these observations, suggested by some of the later experiments in the current program, is the use of the electron microscope. Composites would be made using the ingredients which are to be varied. The cured samples would be placed under stress at the desired temperature. On failure both the failure site and some adjacent areas would be looked at with the electron microscope. Using oxidizer with a narrow particle size distribution an analysis would be made on the nature of the reactions at the oxidizer-fuel interface region, e.g., extent of oxidizer decomposition, extent of breakdown of bonds between oxidizer and fuel, any change in nature of the integrity of the fuel component, etc.

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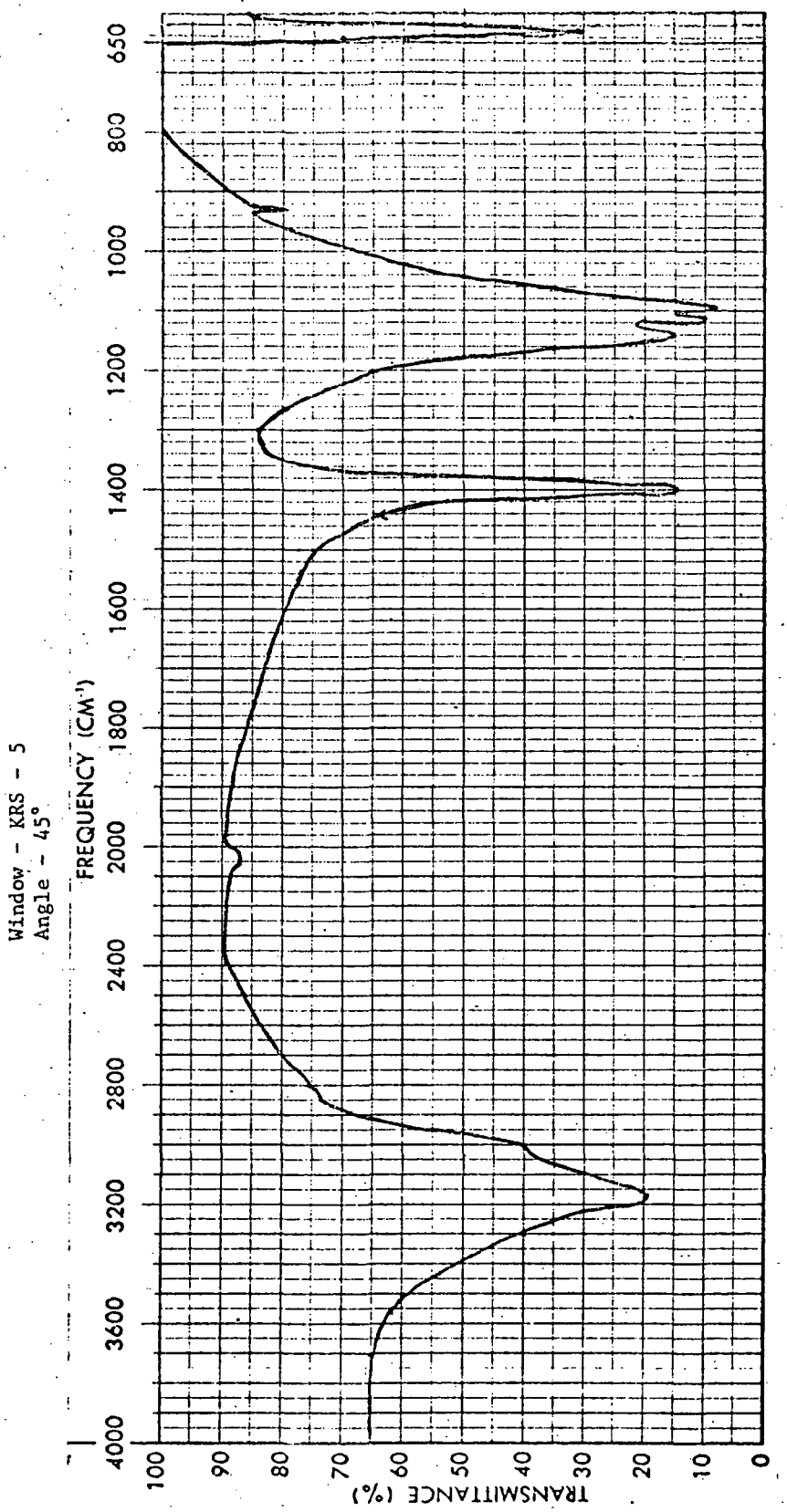
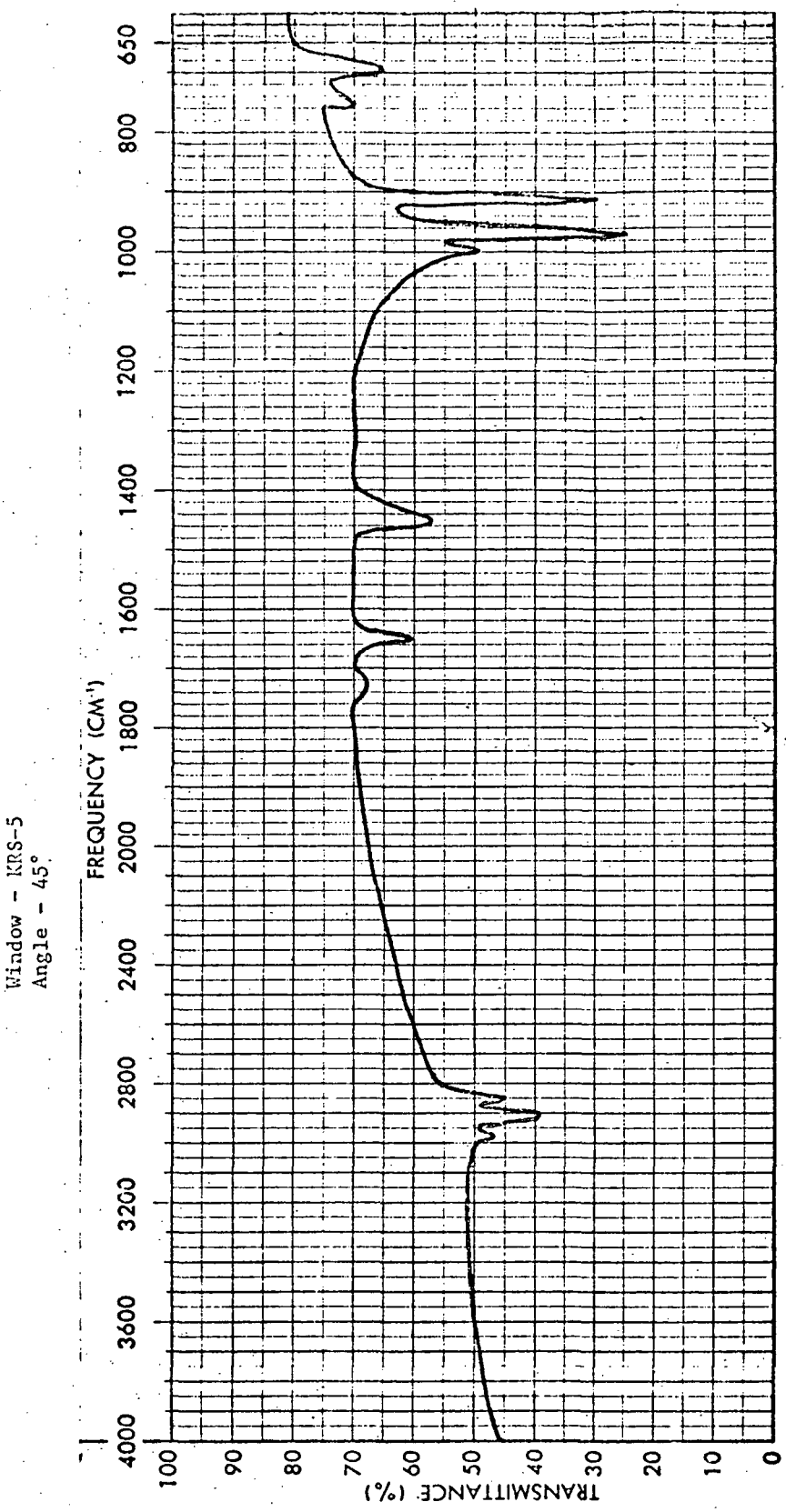



Reflectance IR Spectrum of $NH_4ClO_4$

Figure 1




Reflectance in Spectrum of U·CTPB - BITA

Figure 2

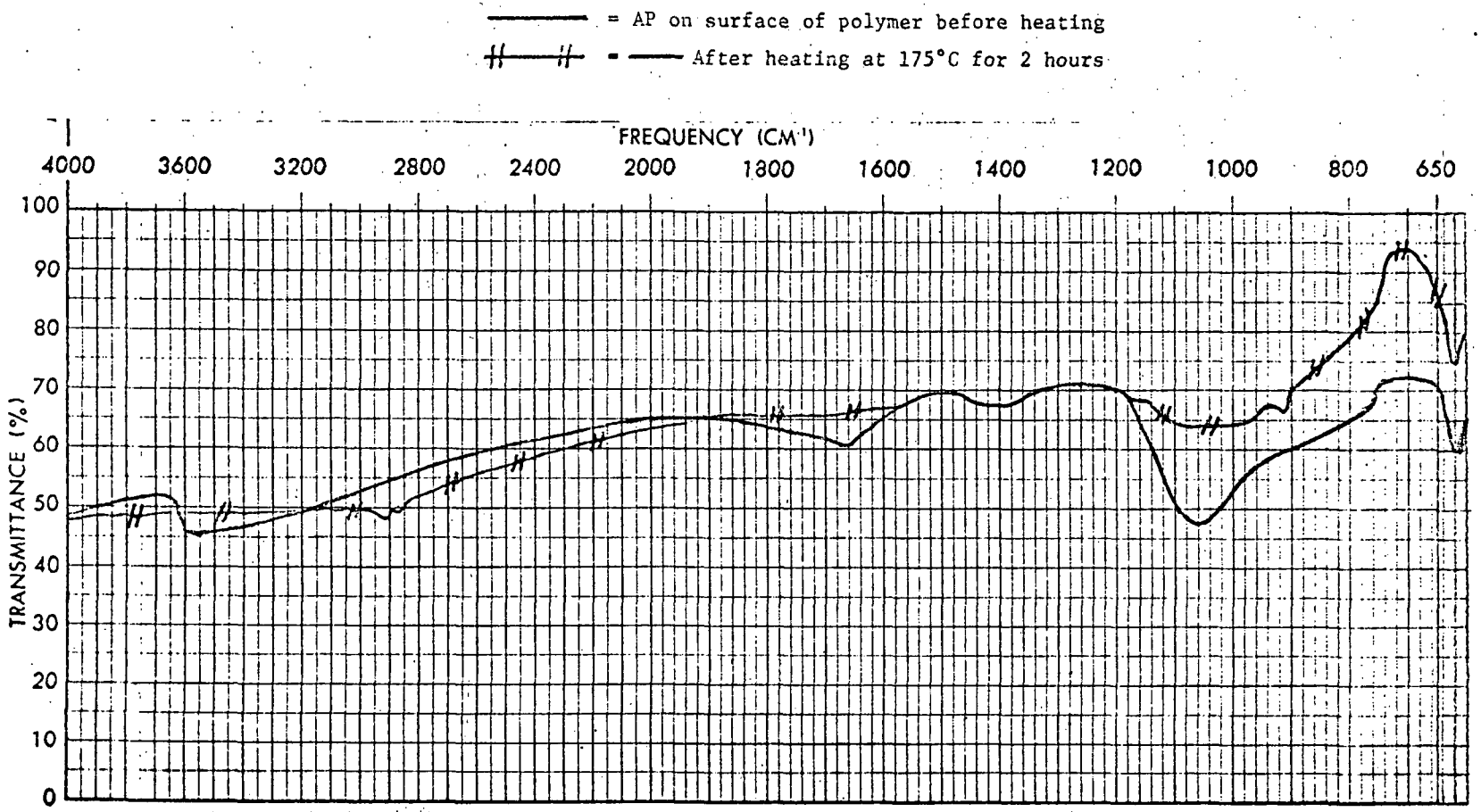
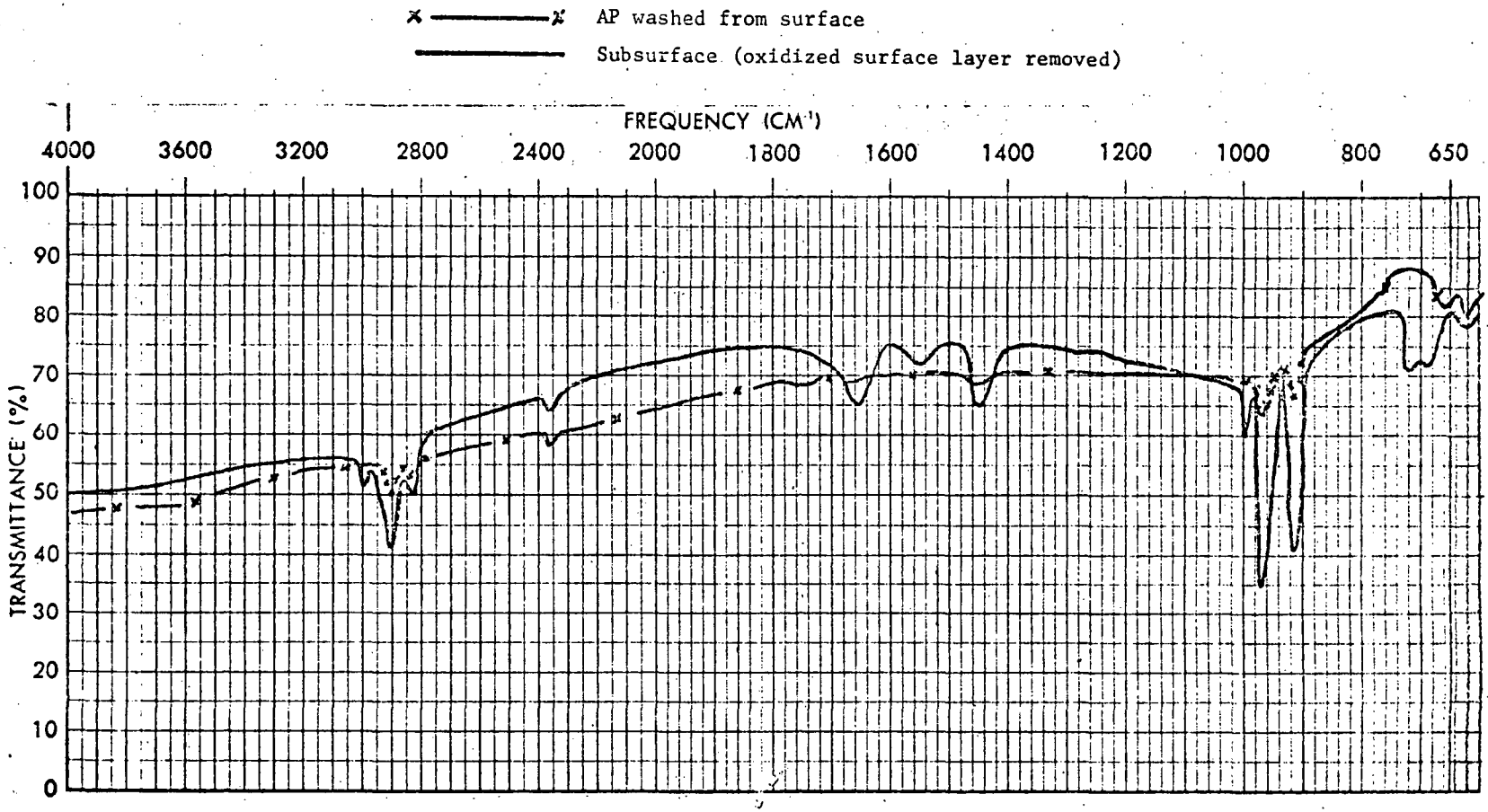



Figure 3

Reflectance IR Spectra of U·CTPB – BITA with $NH_4ClO_4$

Figure 4




Reflectance IR Spectra of U·CTPB - BITA After Oxidation with AP at 175°C for 2 Hours

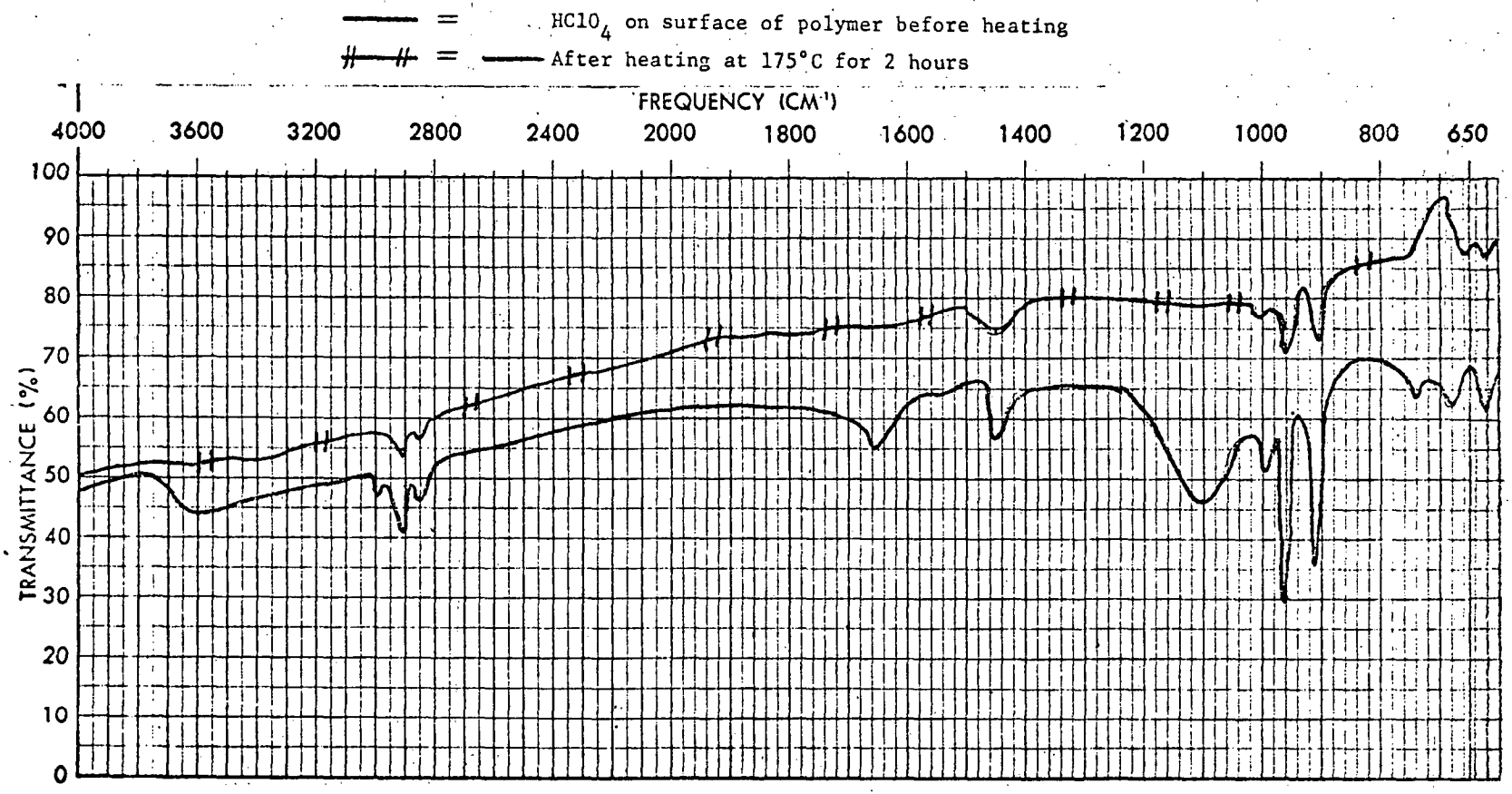
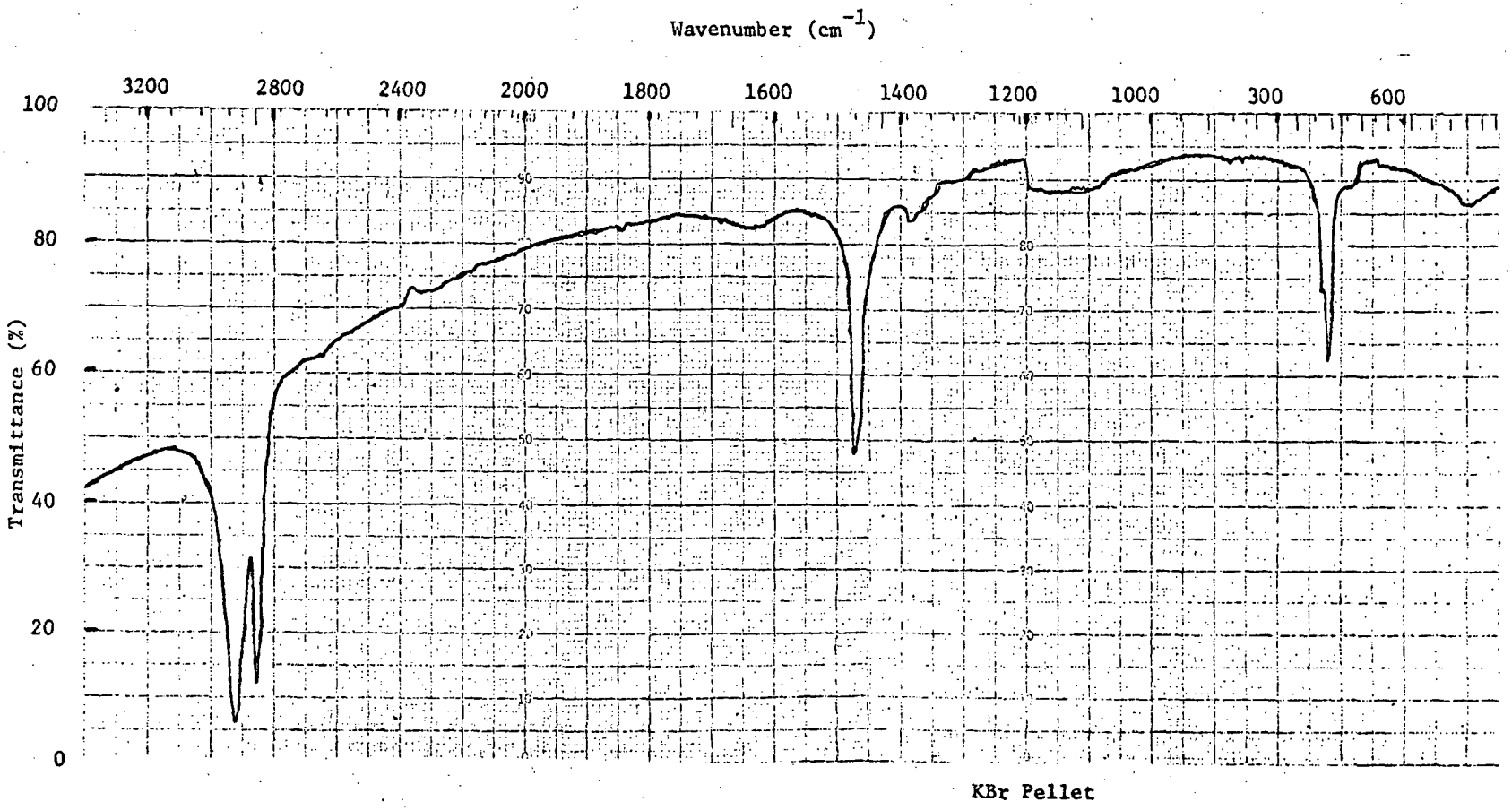



Figure 5

Reflectance IR Spectra of U·CTPB – BITA with $HClO_4$

Figure 6




IR Spectrum of Polyethylene (PE)

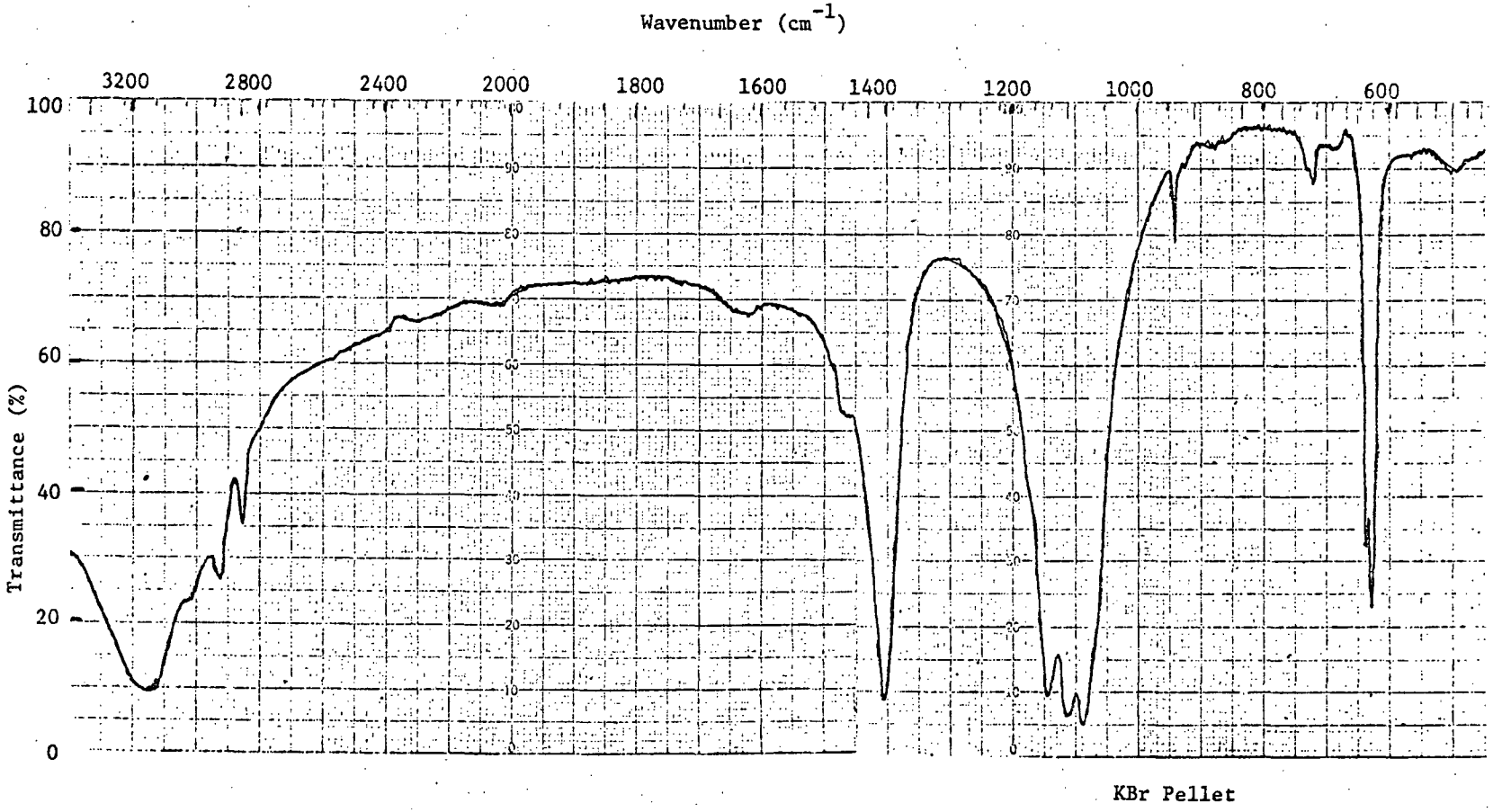
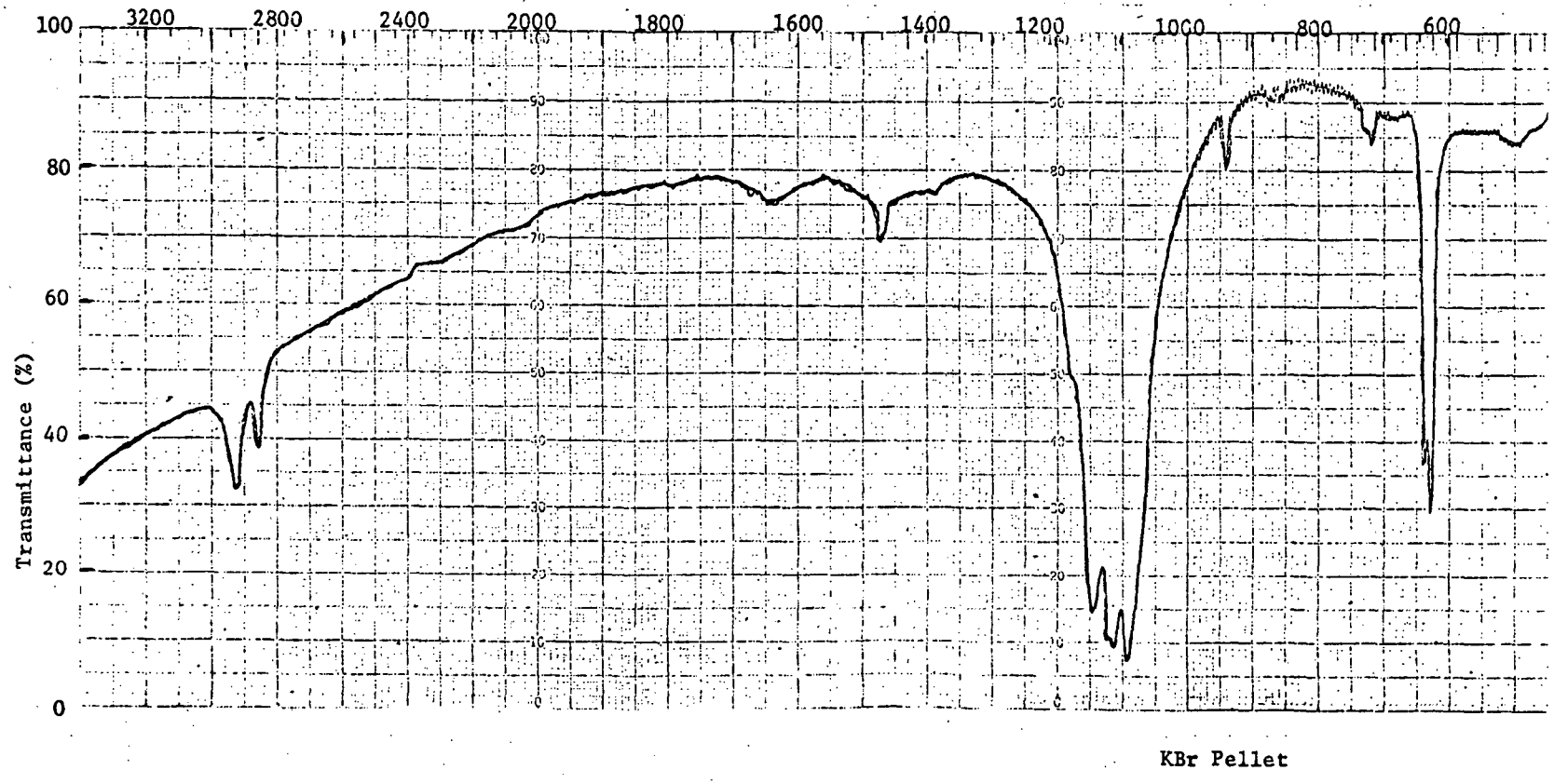



Figure 7

IR Spectrum of 25/75 wt% PE/AP (Recrystallized)

Figure 8




IR Spectrum of 25/75 wt% PE/$KClO_4$

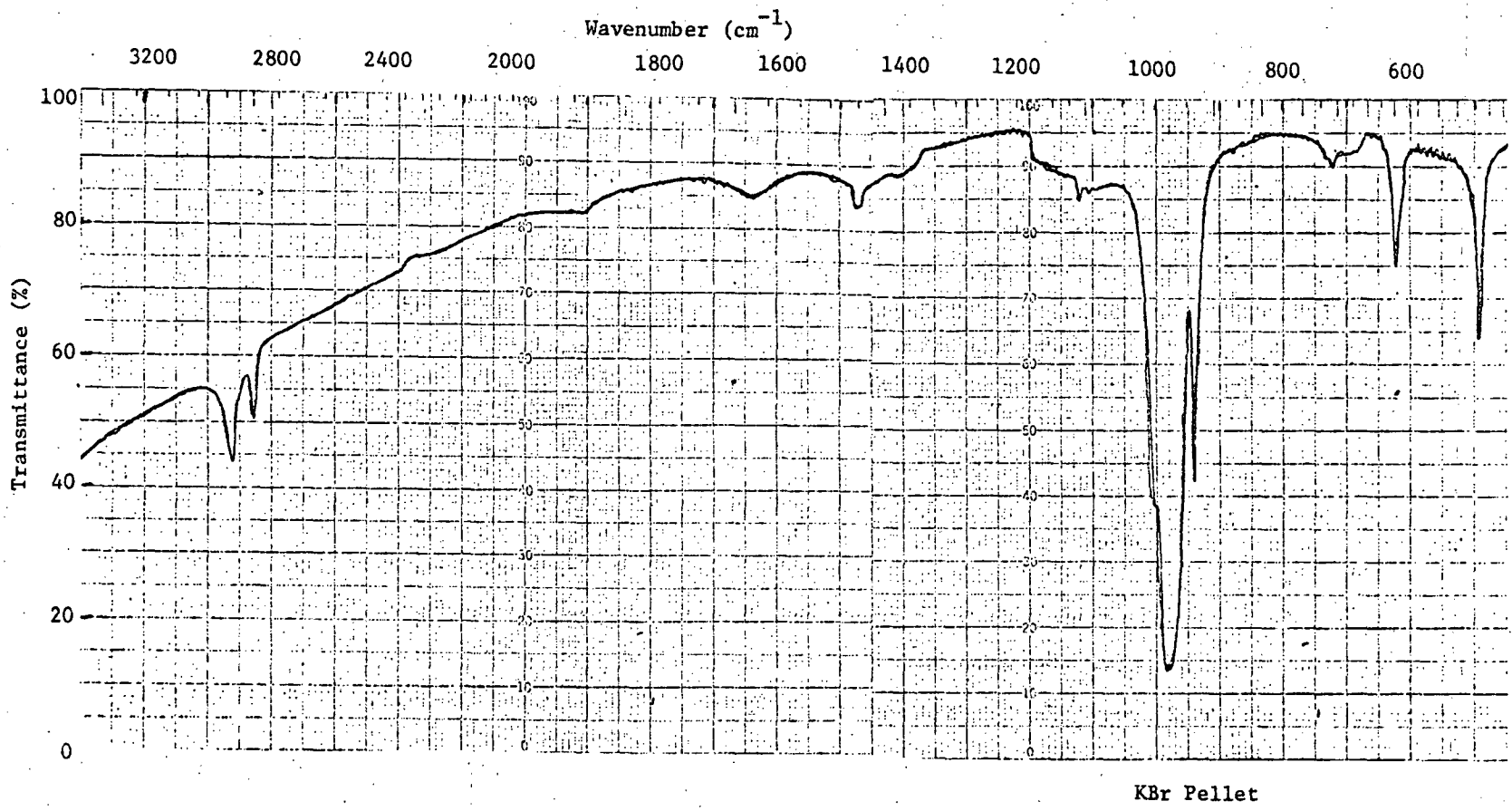
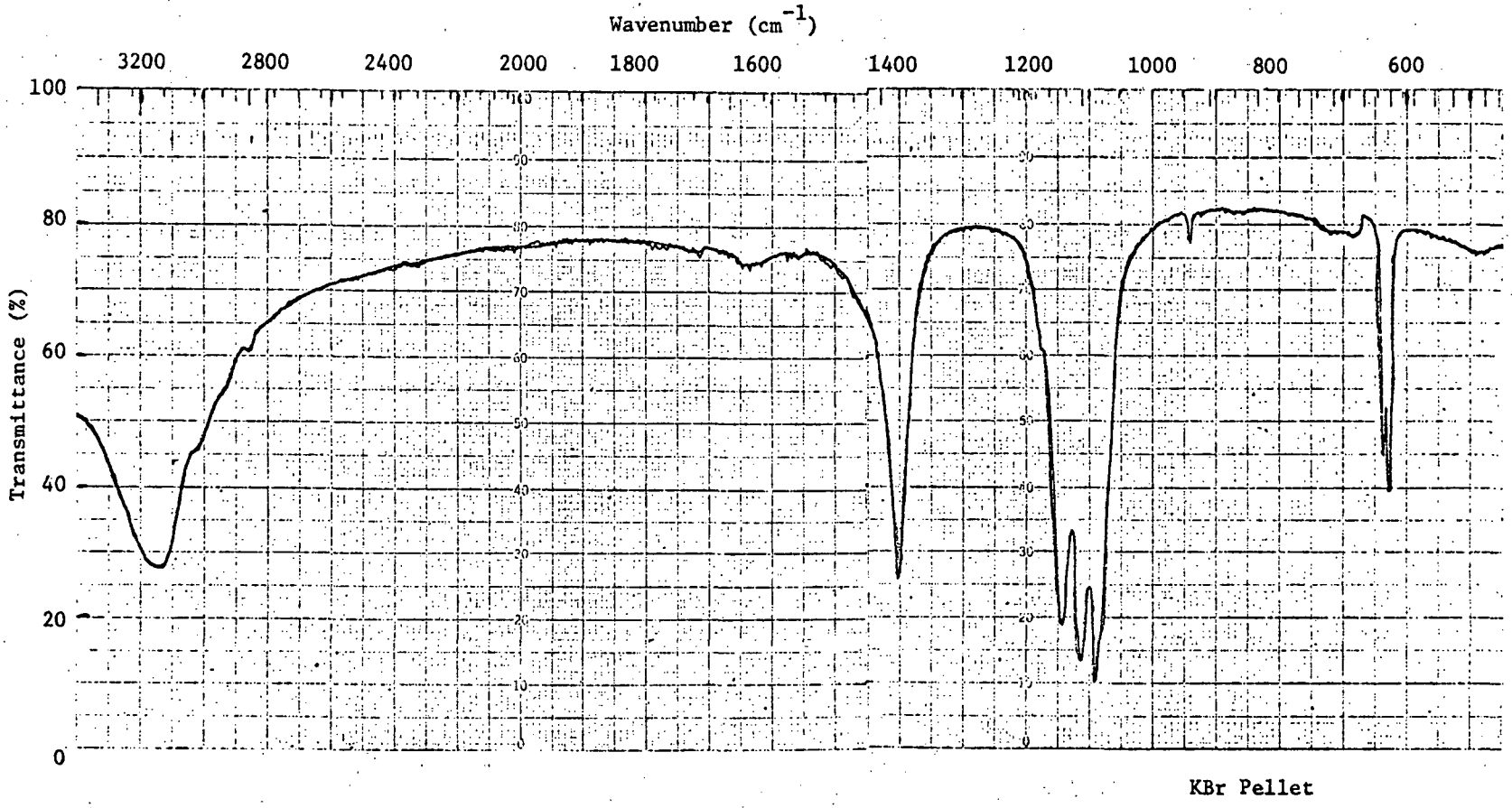



Figure 9

IR Spectrum of 25/75 wt% PE/$KClO_3$

Figure 10




IR Spectrum of 25/75 wt% PE/AP (Recrystallized) After Heating at 170°C for 45 Hours

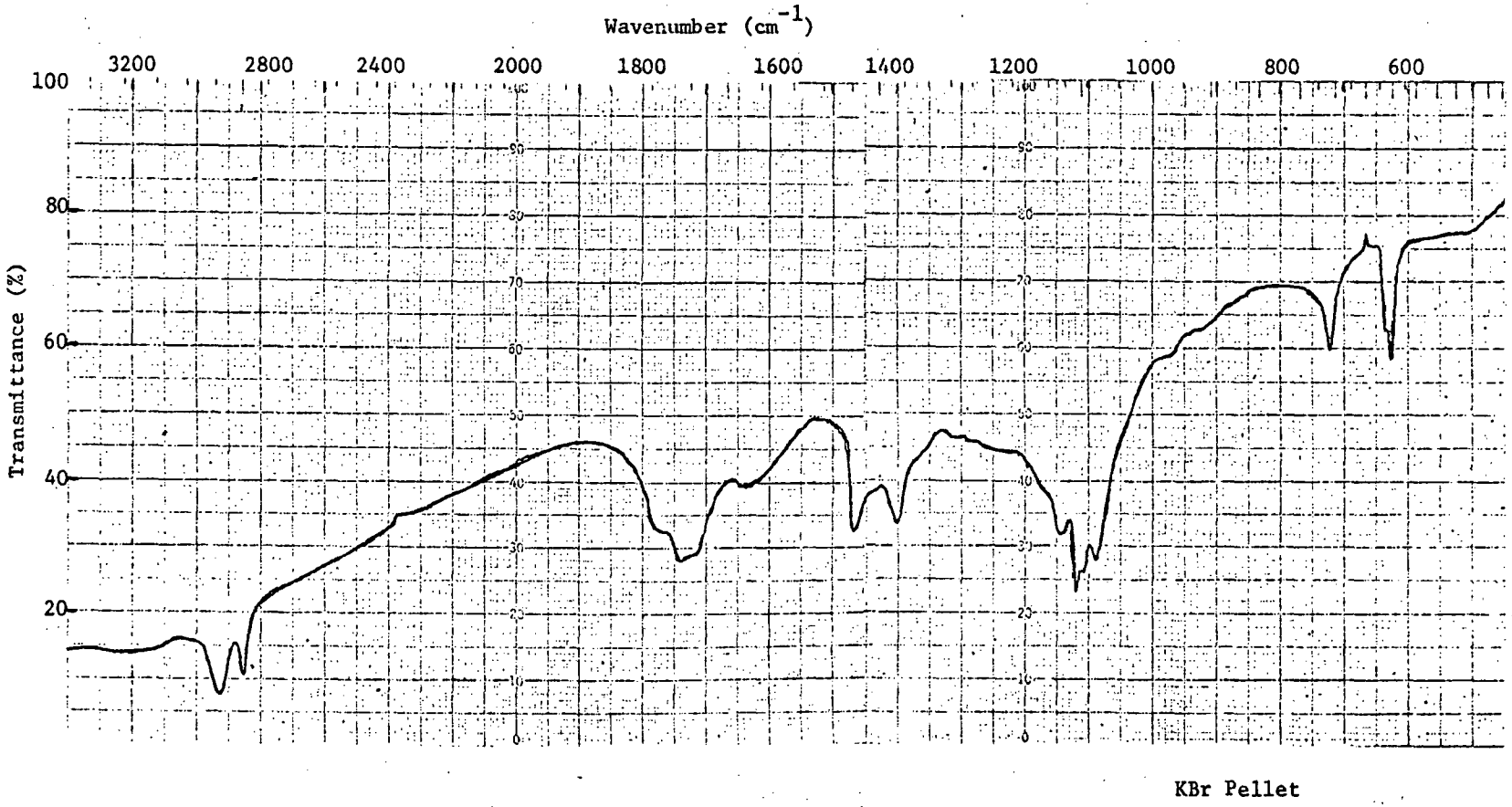
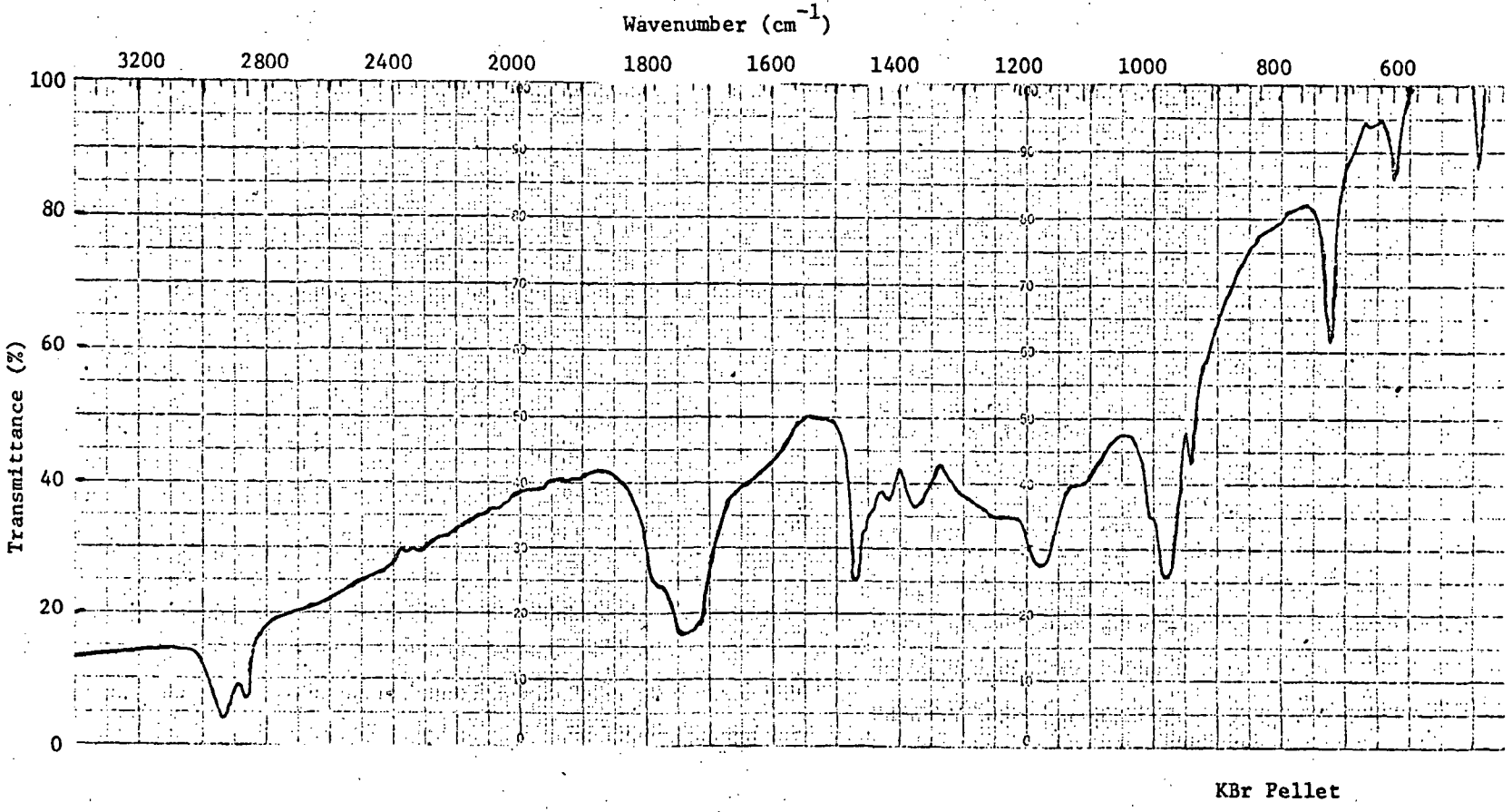



Figure 11

IR Spectrum of Organic Residue from Heating PE/AP (Recrystallized) at 170°C for 45 Hours

Figure 12




IR Spectrum of Organic Residue from Heating PE/$KClO_3$ at 170°C for 8 Hours

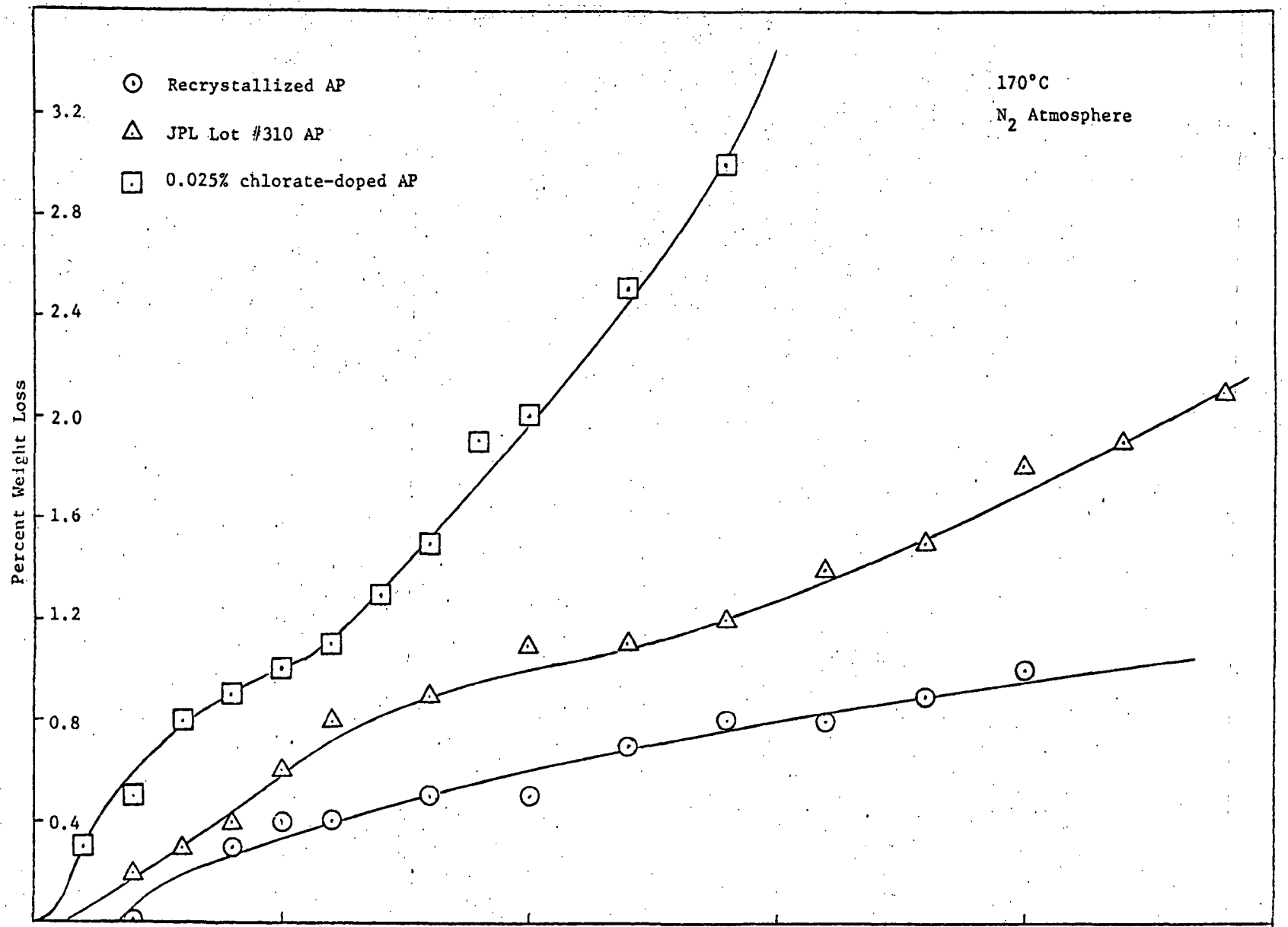
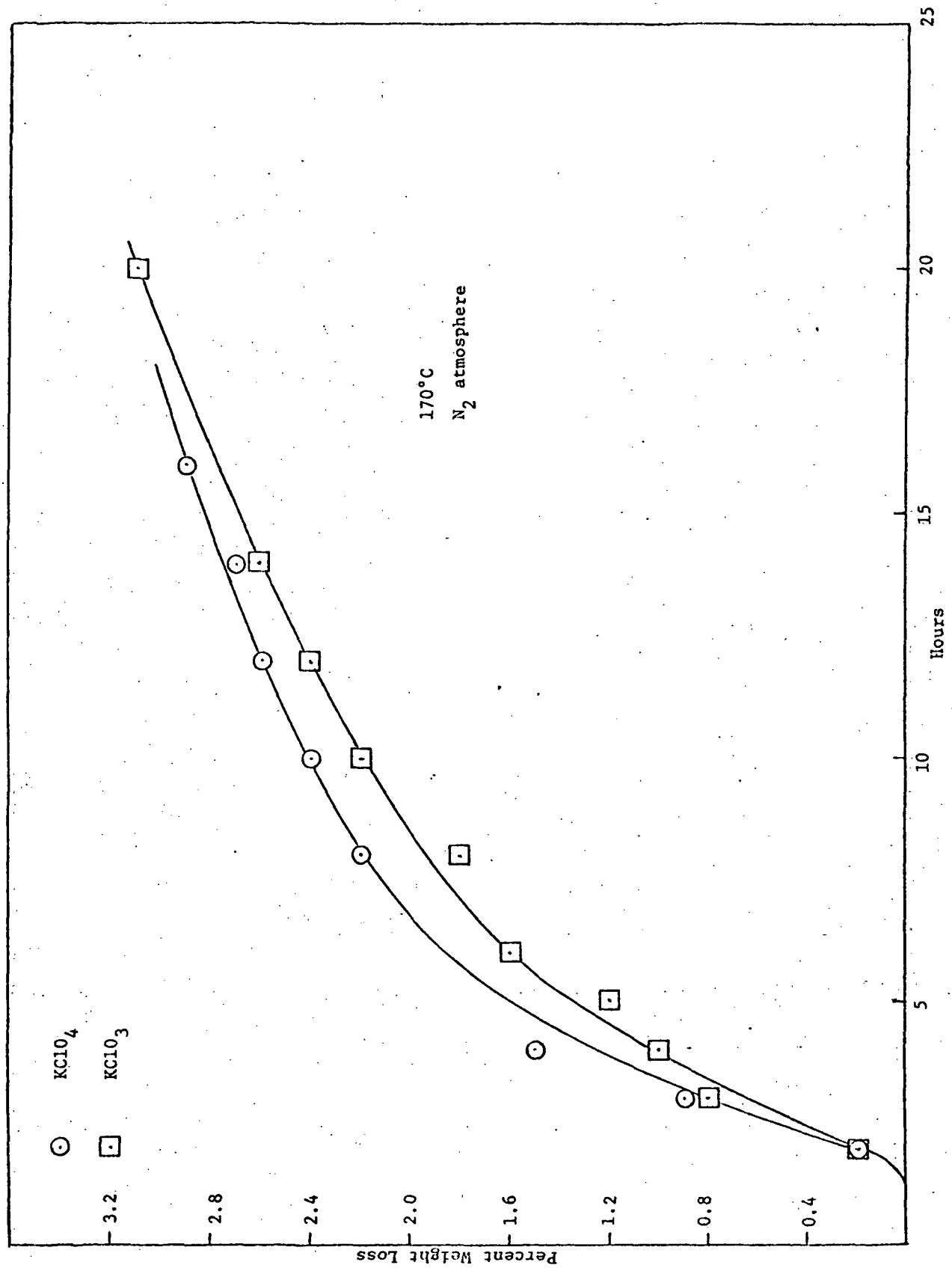


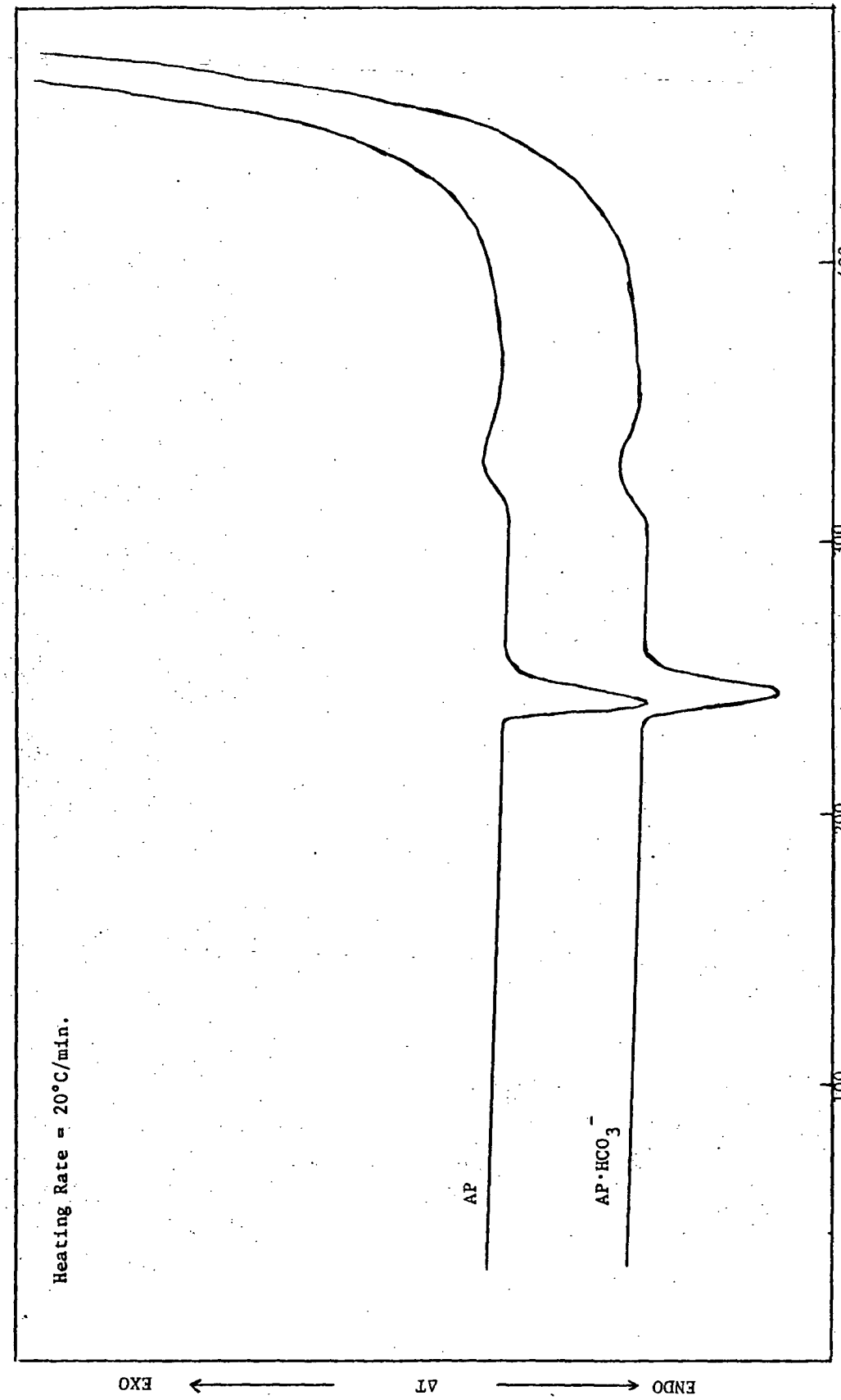

Figure 13

Isothermal Decomposition of PE/AP (25/75) Mixtures




Isothermal Decomposition of PE Oxidizer (25/75) Mixtures

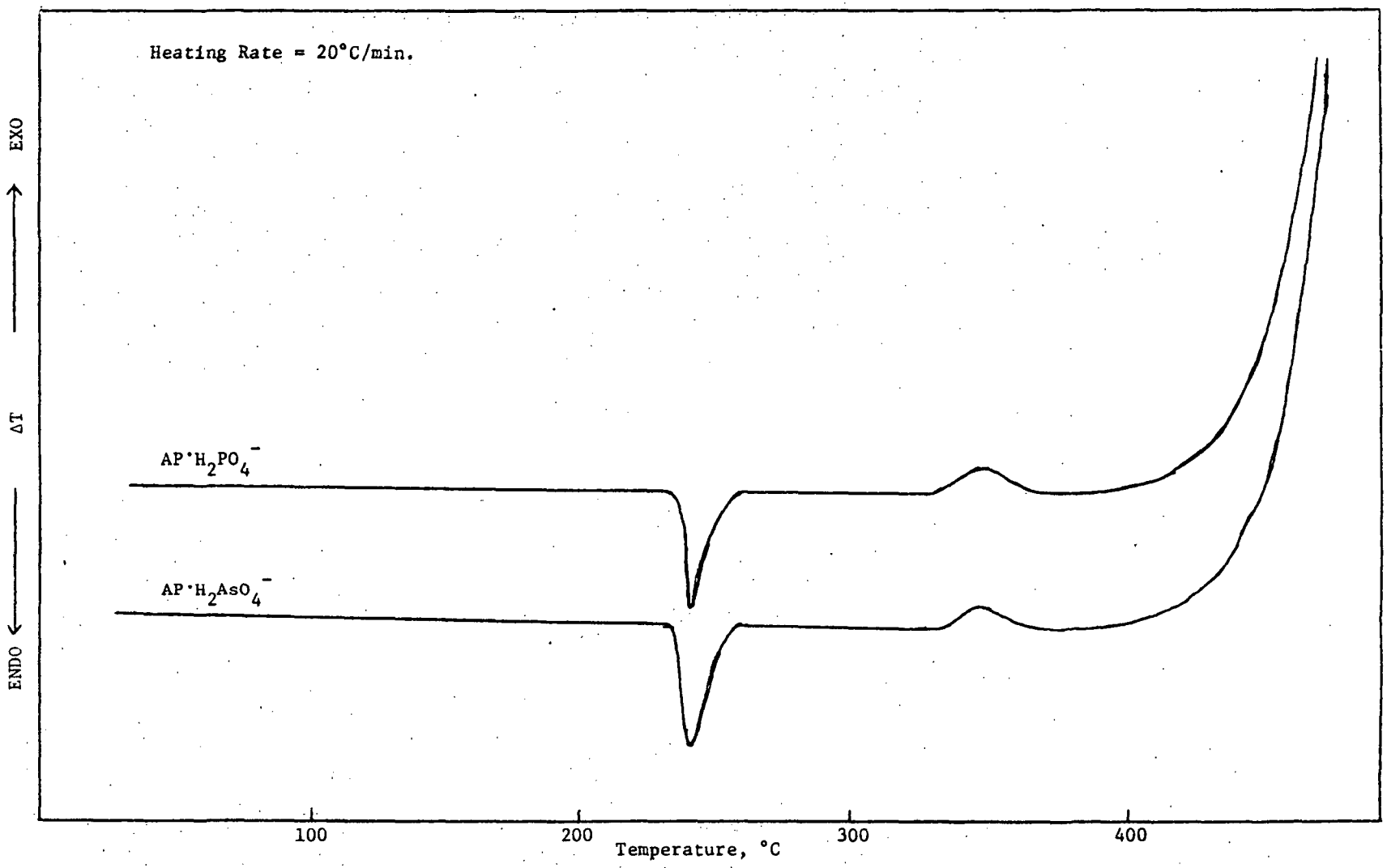
Figure 14



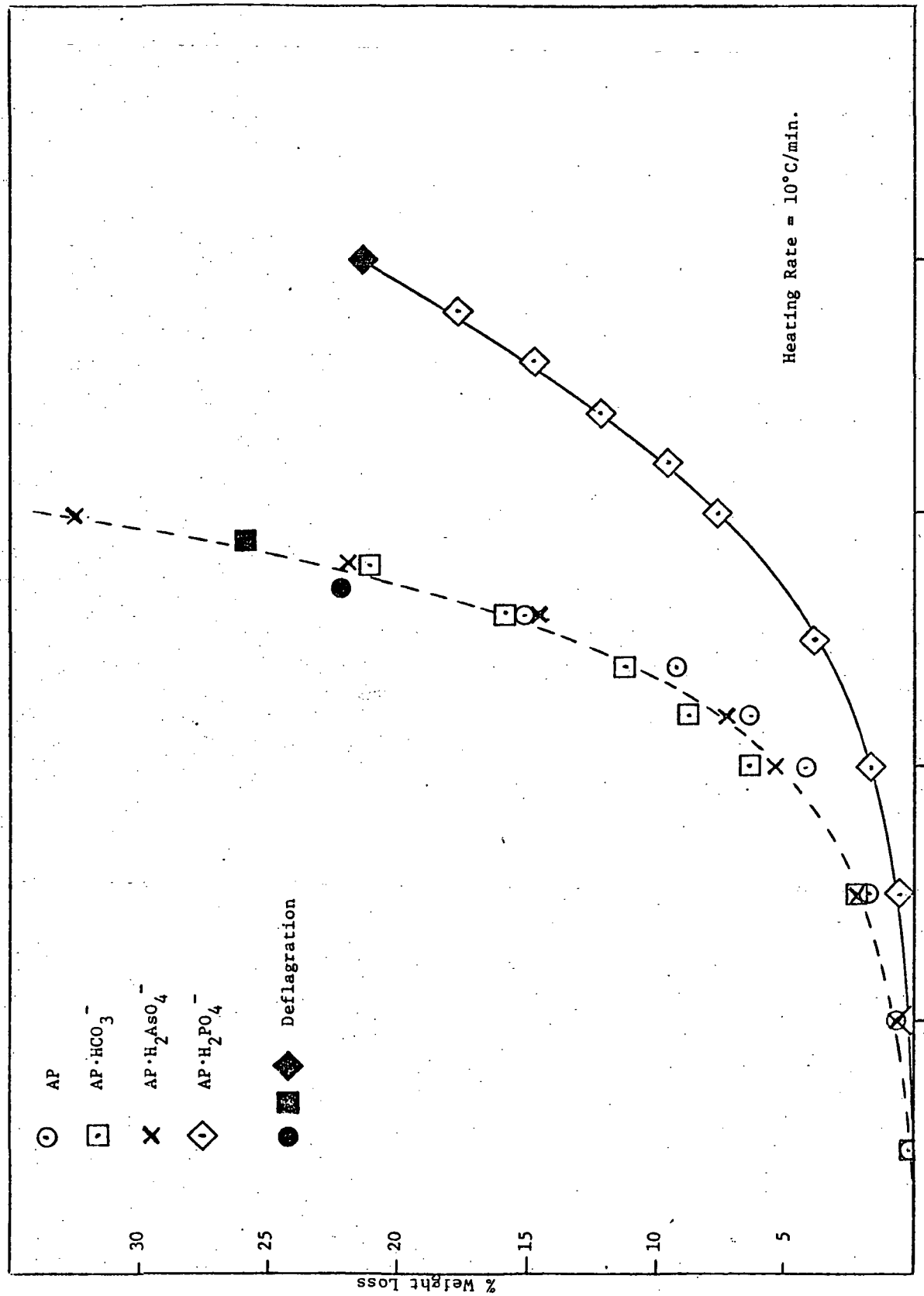

DTA of AP (Recrystallized) and AP·$HCO_3^-$

Figure 15

Figure 16

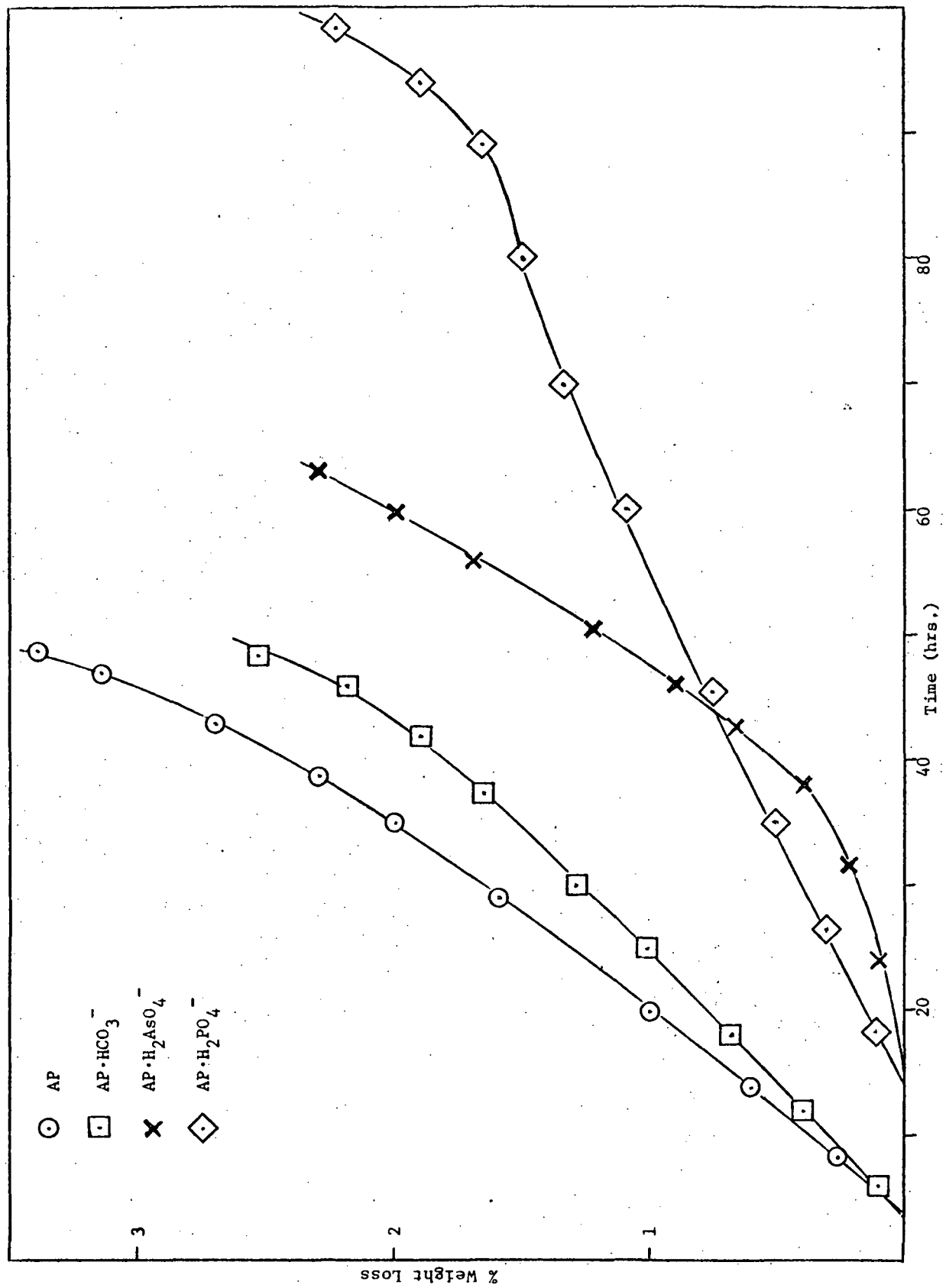



DTA of $AP \cdot H_2PO_4^-$ (0.08%) and $AP \cdot H_2AsO_4^-$ (0.19%)




Thermogravimetric Weight Loss Data on AP/PE (75/25) Composites

Figure 17




Isothermal (170°C) TGA Data on AP/PE (75/25) Composites

Figure 18

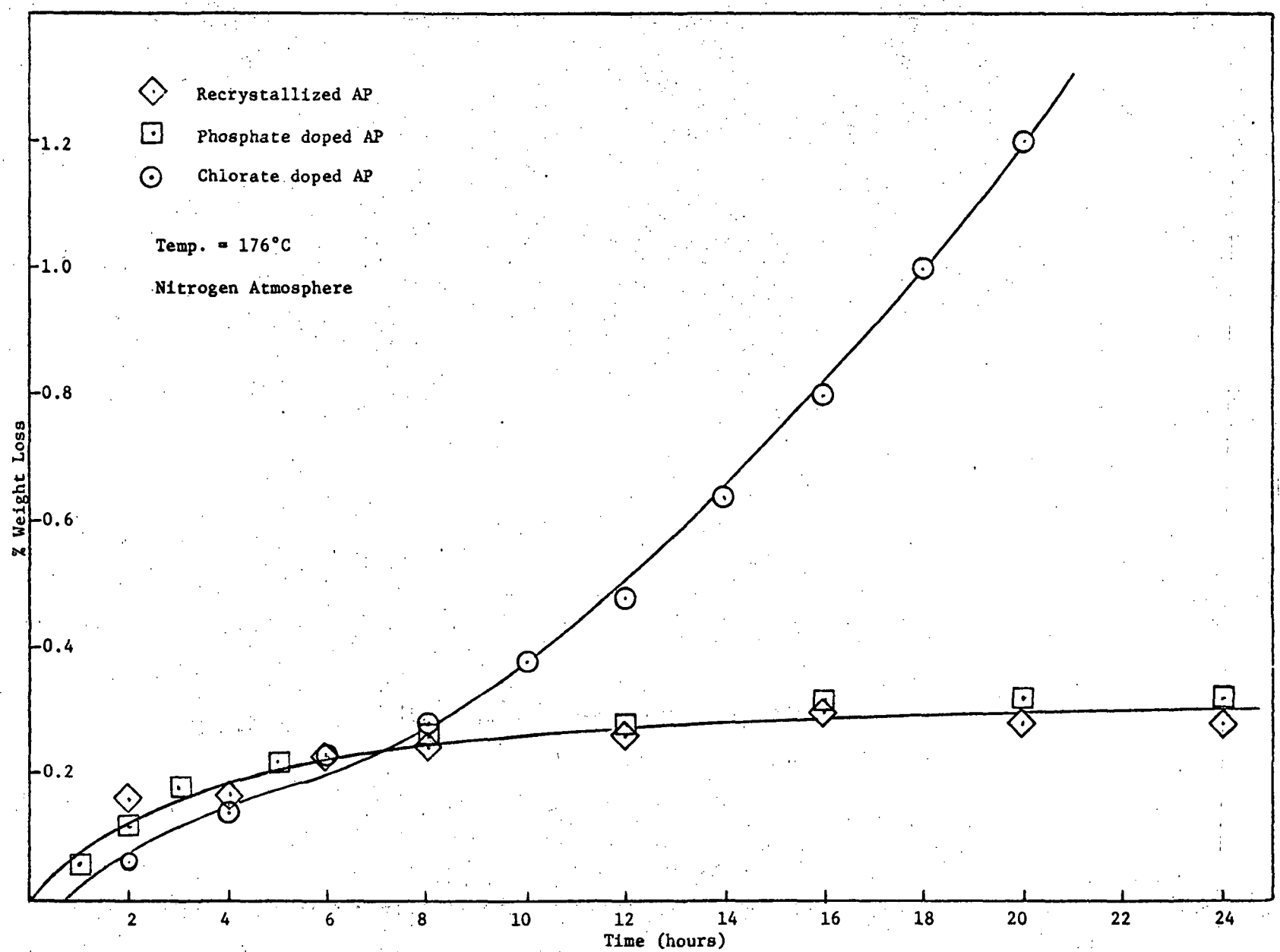
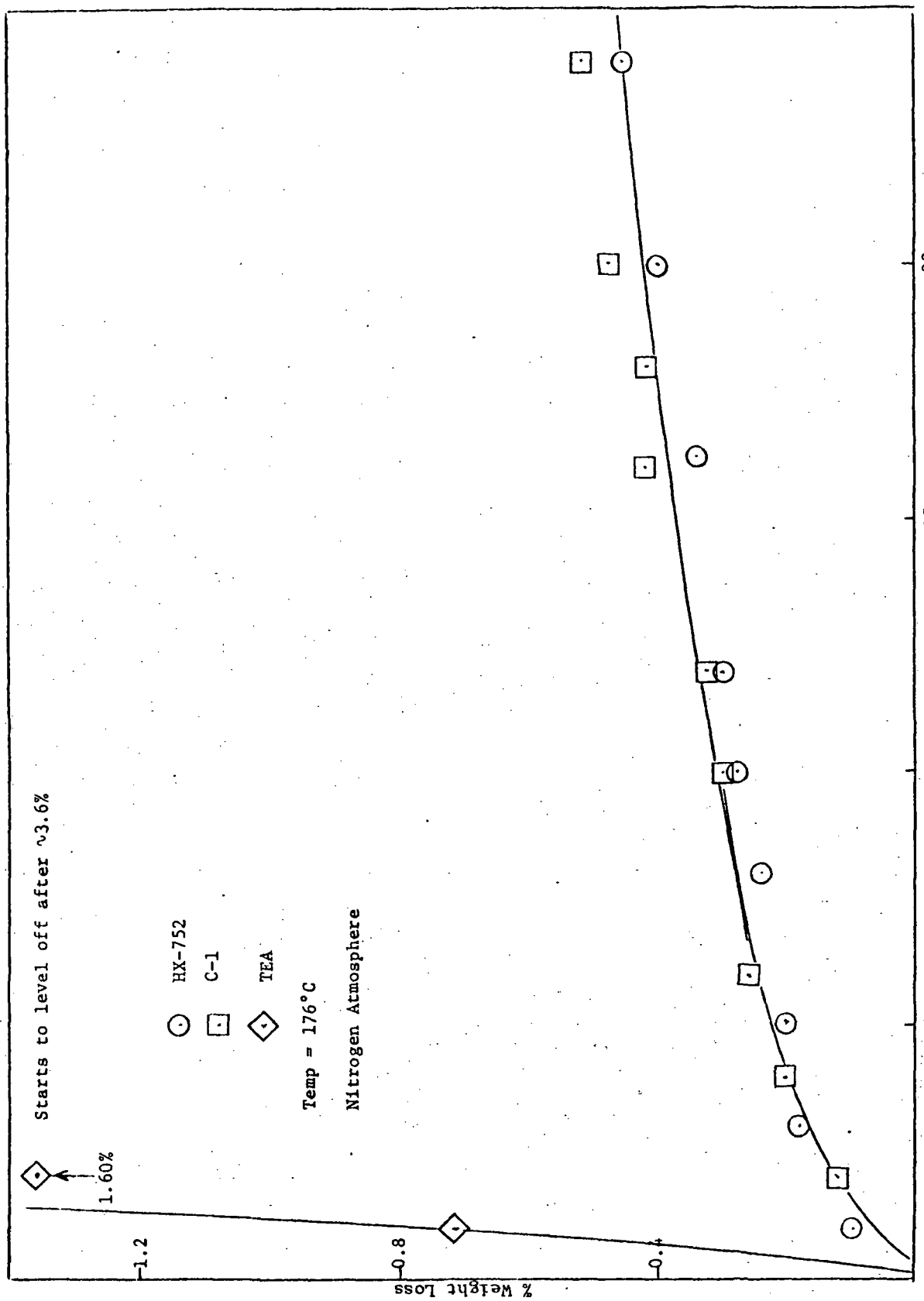



Figure 19

Effect of Oxidizer on the Thermal Stability of AP/Unsaturated Prepolymer (50/50) Mixtures




Effect of Bonding Agents on the Thermal Stability of AP/Unsaturated Prepolymer (50/50) Mixtures

Figure 20

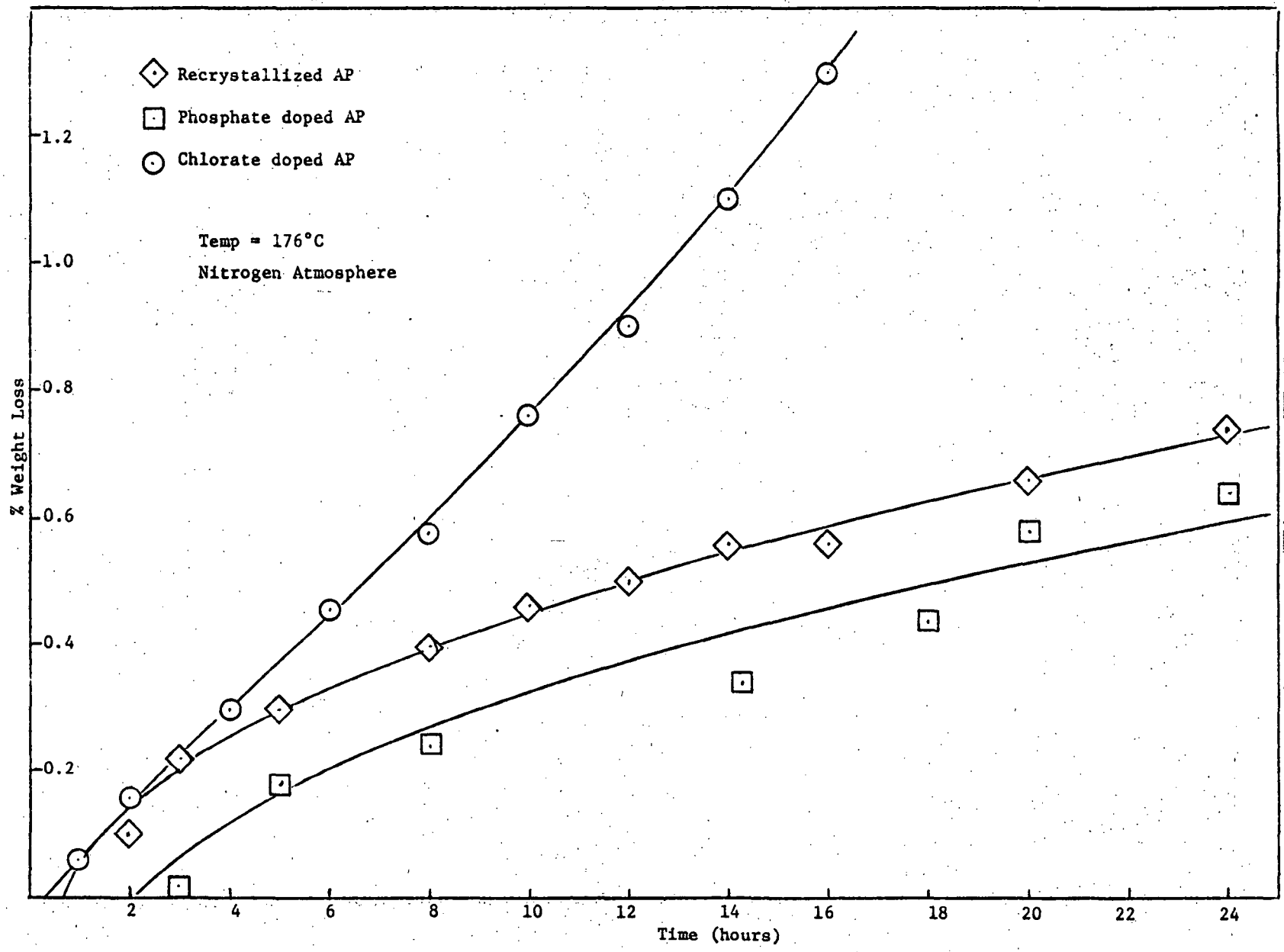
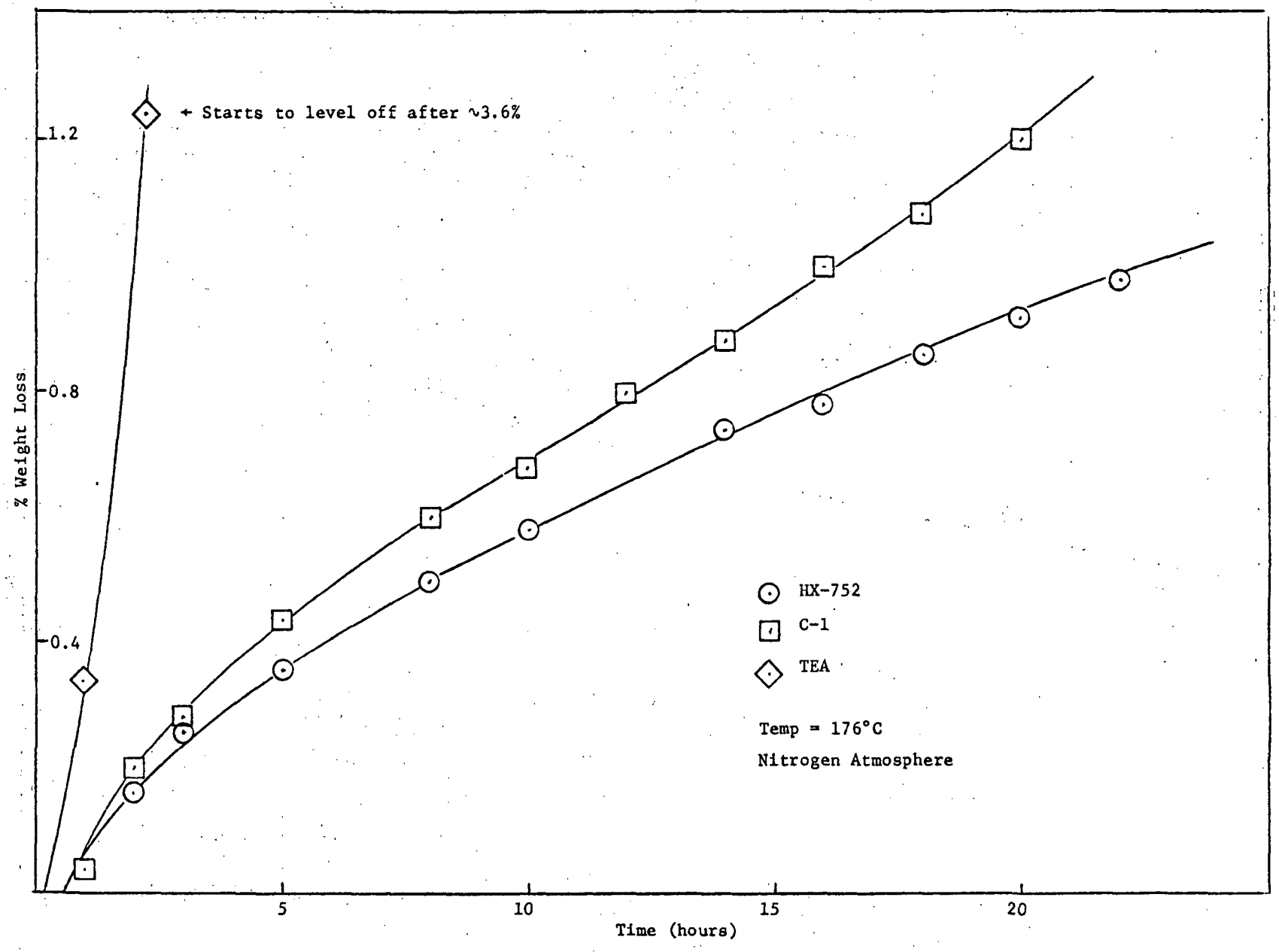


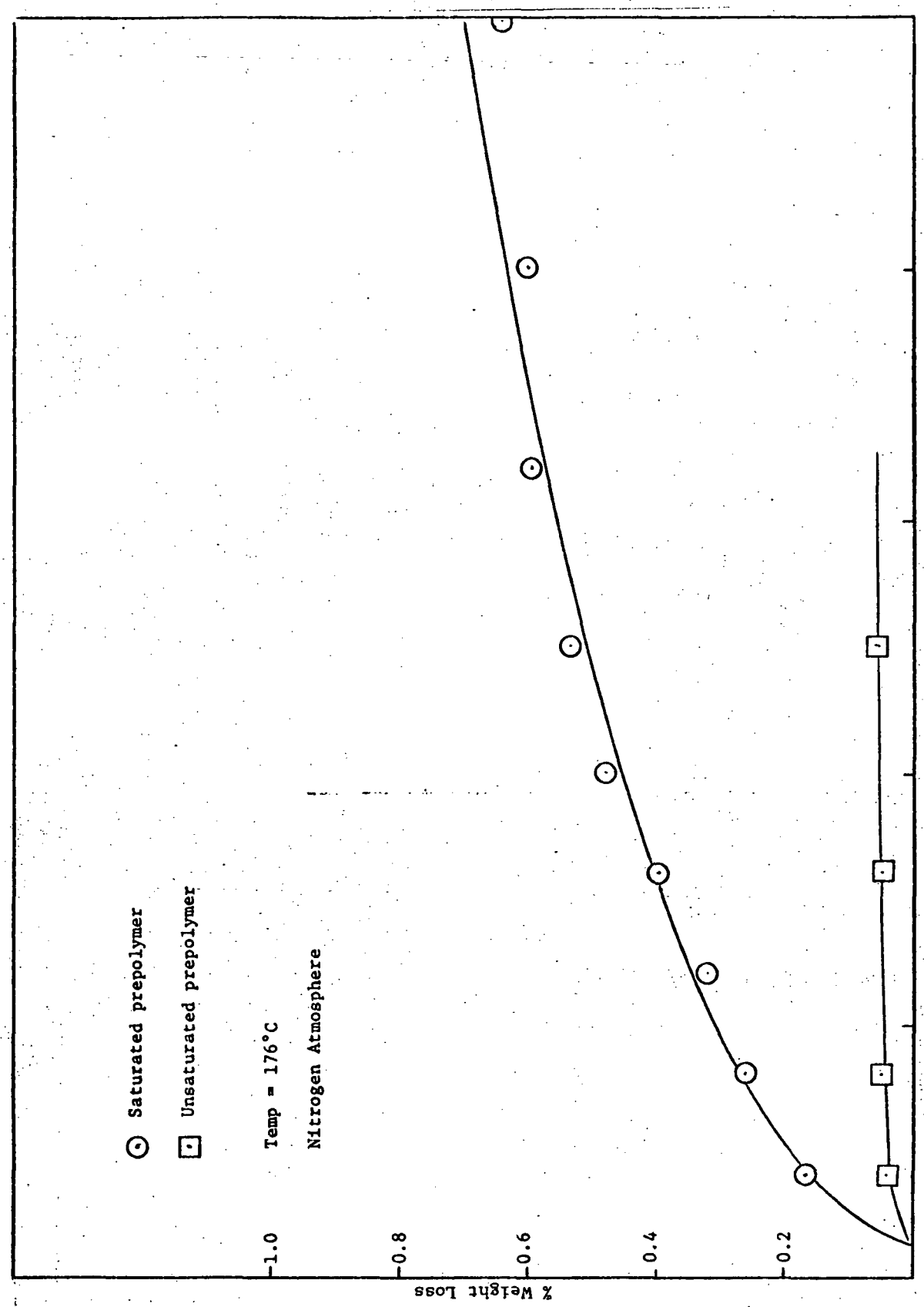

Figure 21

Effect of Oxidizer on the Thermal Stability of AP/Saturated Prepolymer (50/50) Mixtures

Figure 22



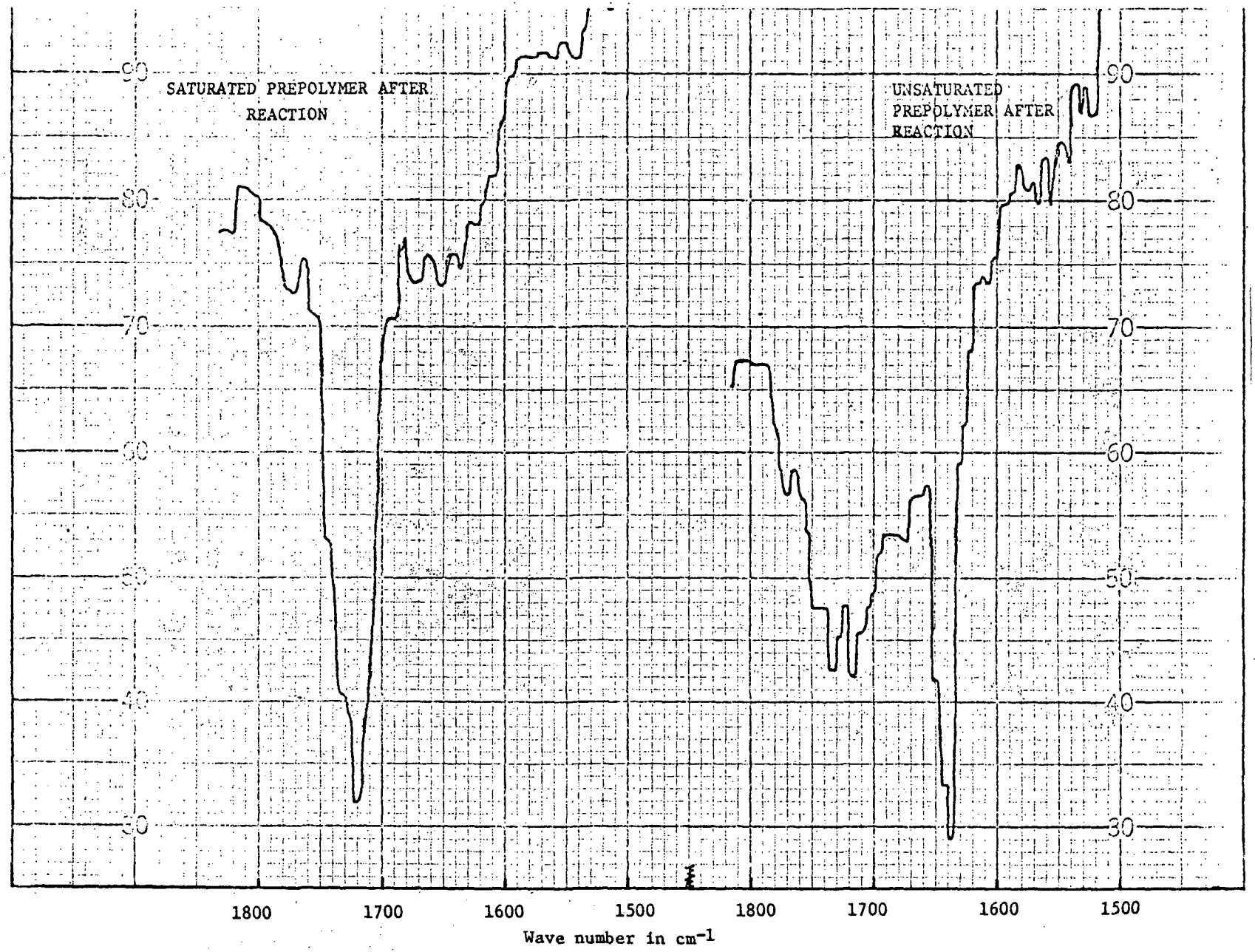

Effect of Bonding Agents on the Thermal Stability of AP/Saturated Prepolymer (50/50) Mixtures

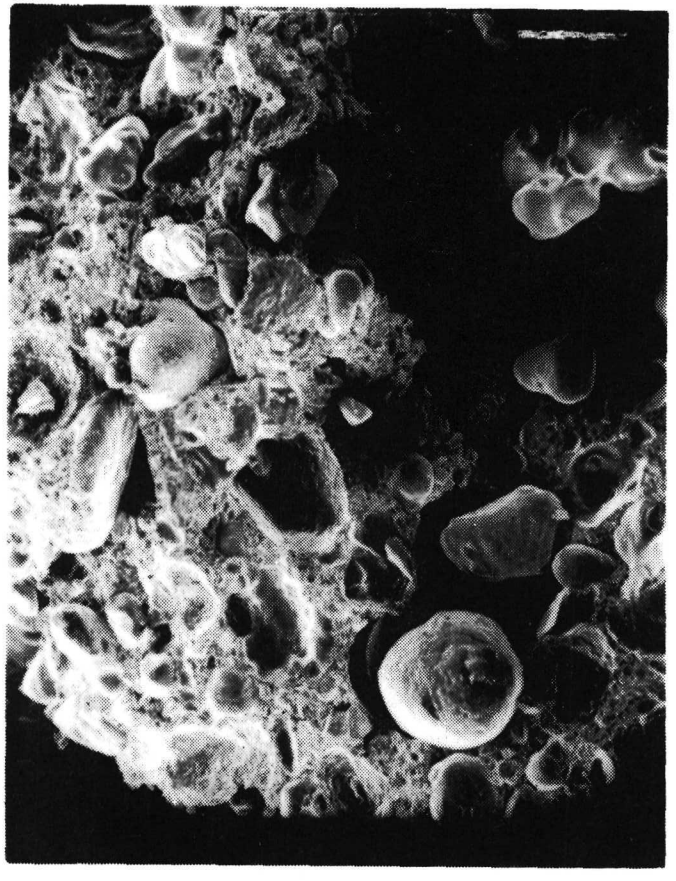



Thermogravimetric Weight Loss Data on a Saturated and an Unsaturated Hydrocarbon Polymer

Figure 23

Figure 24


SATURATED PREPOLYMER AFTER REACTION
UNSATURATED PREPOLYMER AFTER REACTION
90
80
70
60
50
40
30
1800
1700
1600
1500
Wave number in cm-1



After Eight Cycles
x 50

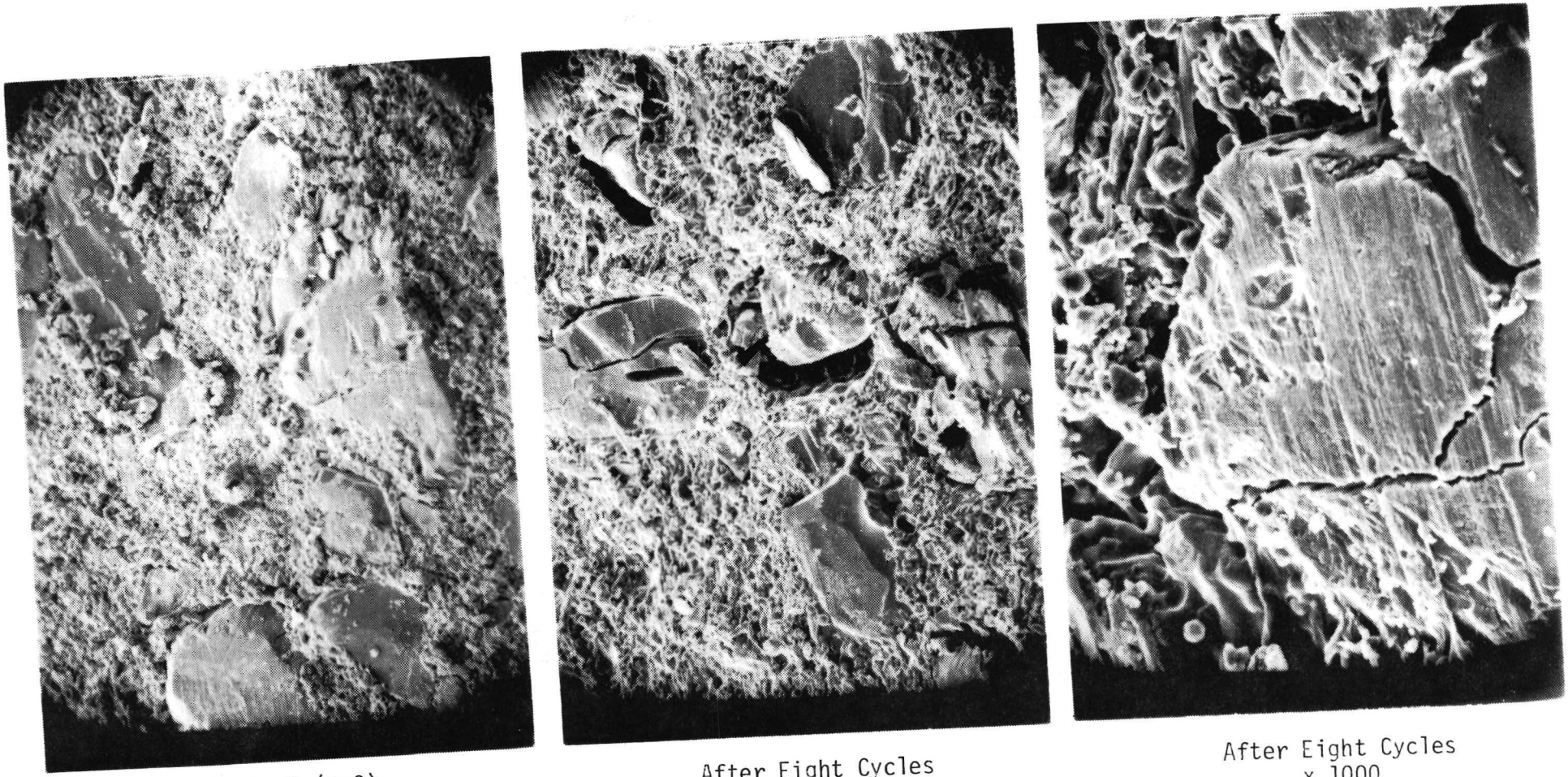
After Eight Cycles
x 500

Propellant 73-30-70 (p14) - Samples are of Failure Area (not a cut surface)

Figure 25

Electron Microscope Photographs of Heat Sterilized Propellant

Figure 26



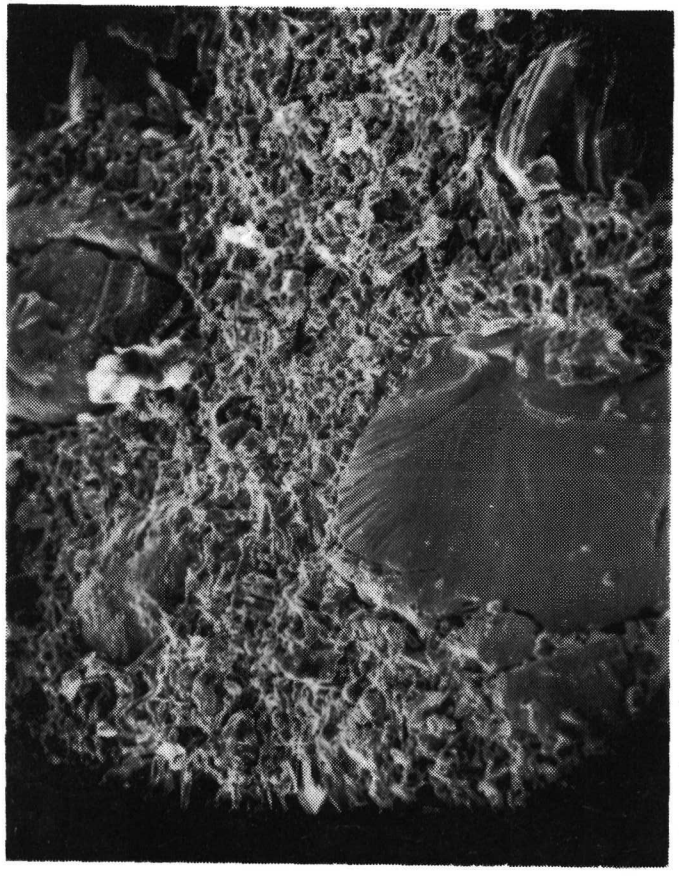
Control (t=0)
x 100

After Eight Cycles
x 200

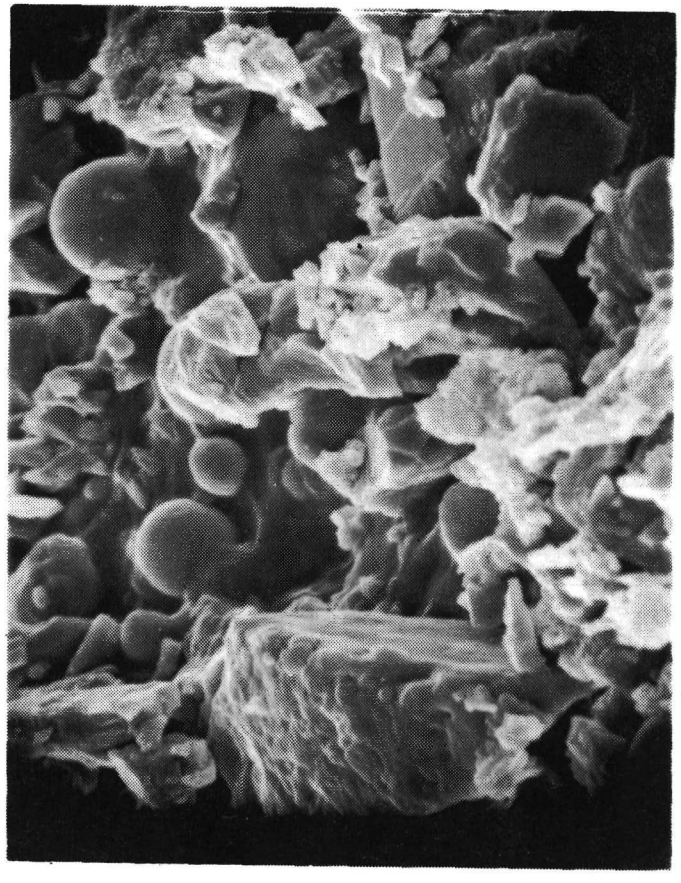
After Eight Cycles
x 1000

Propellant 73-30-70 (p14) - Samples cut from Edge of Propellant Grain

Electron Microscope Photographs of Heat Sterilized Propellant



After Eight Cycles
x 200



After Eight Cycles
x 2000

Propellant 73-05-121 (p15) - Samples Cut from Edge of Propellant Grain

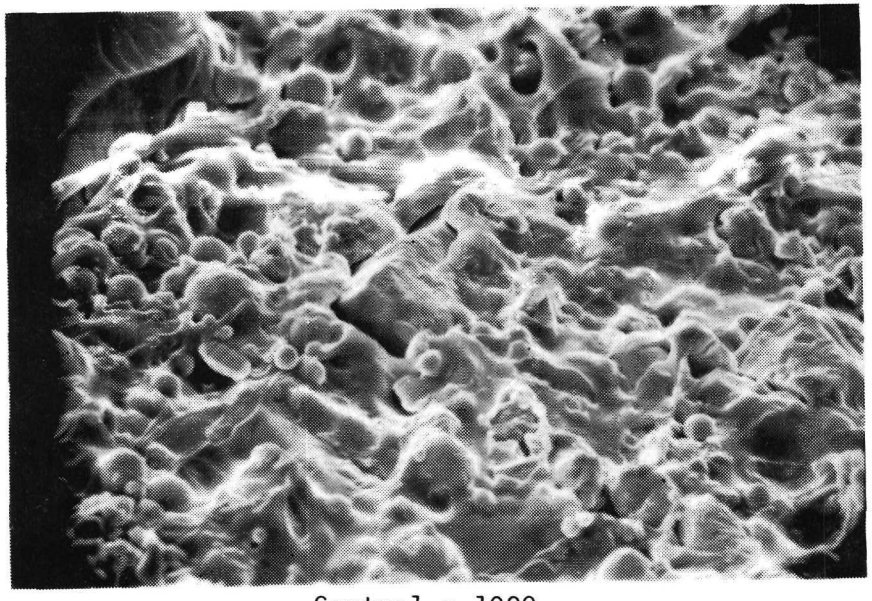
Electron Microscope Photographs of Heat Sterilized Propellant

Figure 27

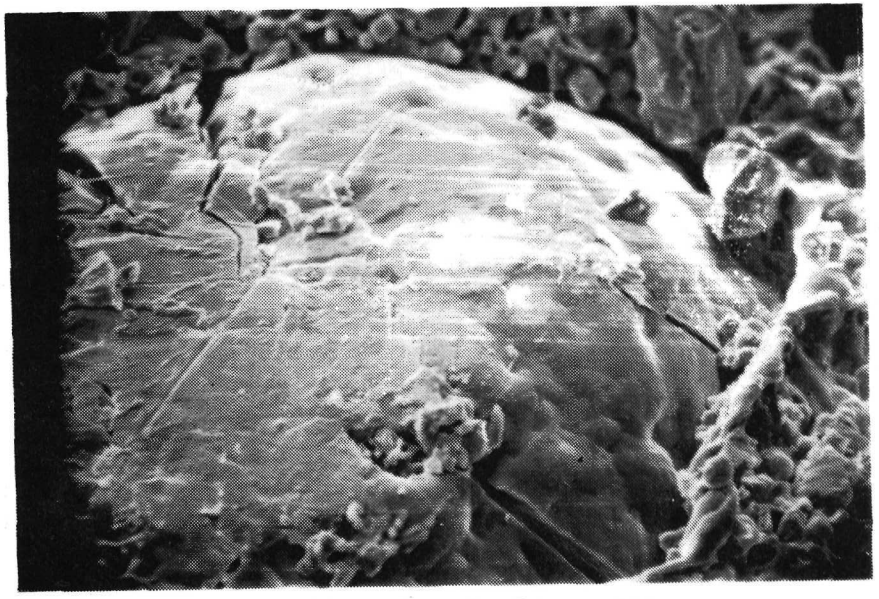
Figure 28

Control x 100

After Two Cycles x 100



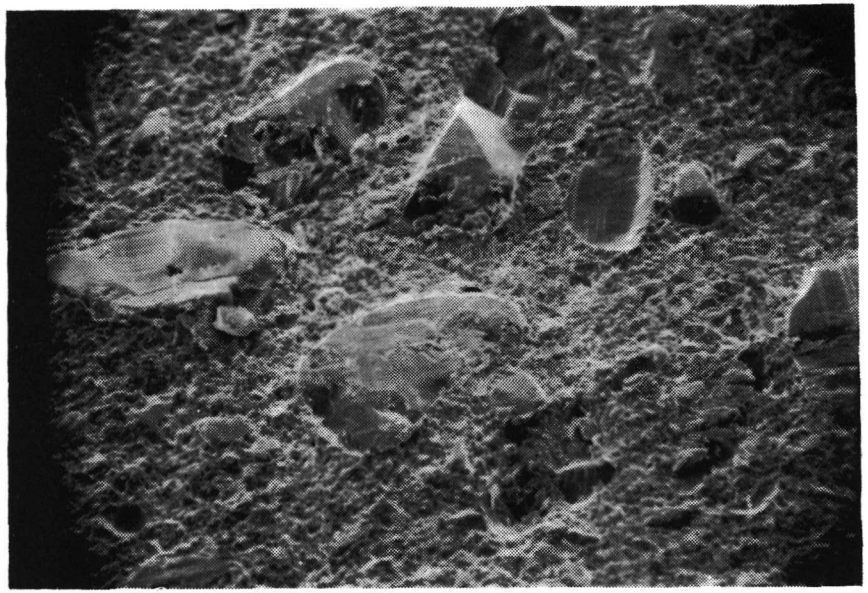
Control x 1000



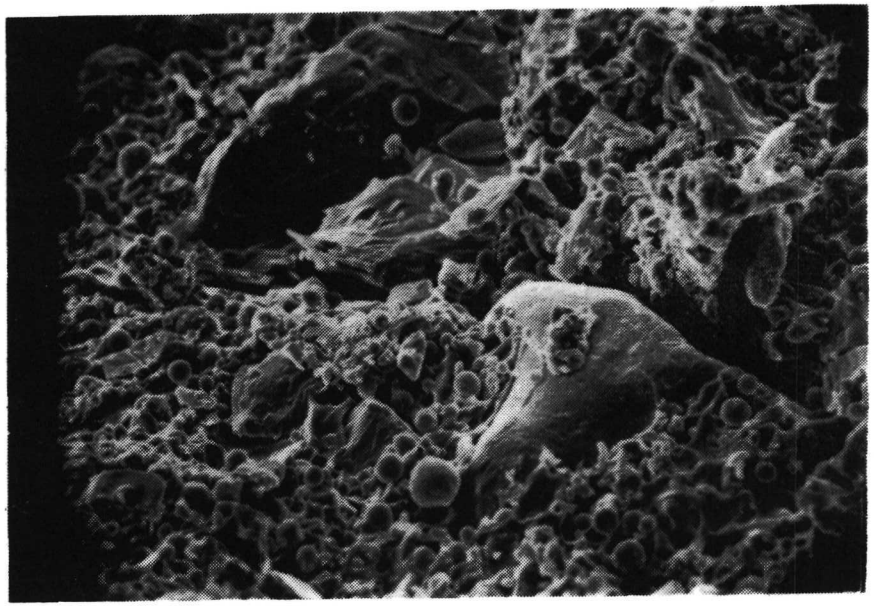
After Two Cycles x 500

Propellant 73-30-82 (p15) - Samples Cut from Edge of Propellant Grain

Electron Microscope Photographs of Heat Sterilized Propellant

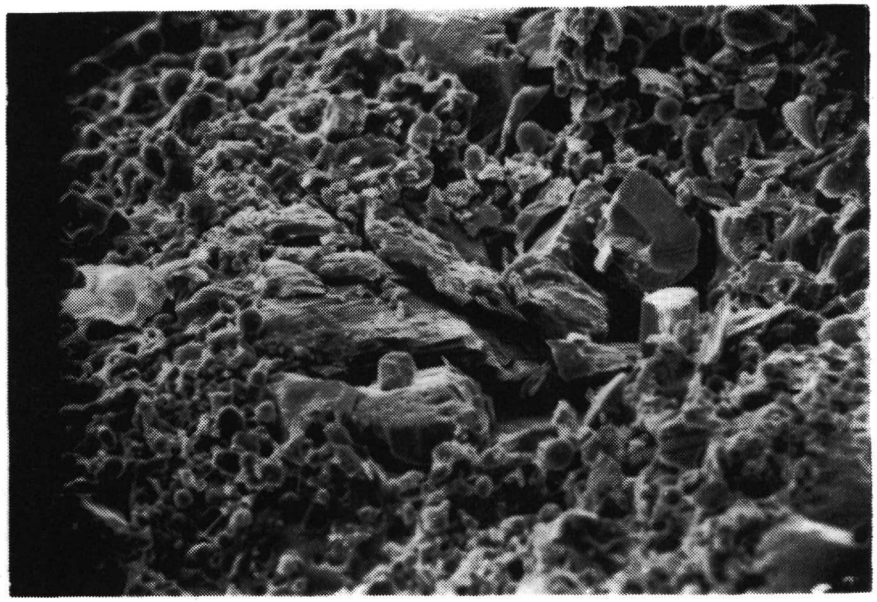


Control x 100



After Two Cycles x 500

After Two Cycles x 100



After Two Cycles x 500

Propellant 73-30-75 (p15) - Samples Cut from Edge of Propellant Grain

Electron Microscope Photographs of Heat Sterilized Propellant

Figure 29