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DEVELOPMENT

SPECIAL REPORT

FOR

SANDIA CORPORATION

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G. L. Clink

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DISCLAIMER

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EXPLOSIVE MATERIAL QUALIFICATION

CHEMISTRY

Chemical and physicochemical aspects of the behavior of CATCP (Sandia Lot 3-3-I) under various thermal and system boundary conditions.

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Special Report

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ABSTRACT

A study of physicochemical and physical characteristics of CATCP (Sandia Lot 3-3-I) indicates that 'Modified CATCP' is obtained only by thermal conditioning in an open system. Differential thermal analyses show the material to be in a dynamic state at 100° and 120°C, continuing on after 168 hours; whether this condition persists at lower temperatures has not yet been determined.

The surface area rate of change continues on at a substantial value at 120°C beyond 168 hours, whereas the rate approaches zero for the 100°C material in the time region from 168 to 336 hours.

DISCUSSION

Initial Evaluation of CATCP (3-3-I)

An initial investigation of the physicochemical properties of CATCP (Sandia Lot 3-3-I) was undertaken to gain some insight into the nature of the material prior to and during its thermal conversion to the desired material, presently referred to as 'Modified CATCP'.

Infrared spectral analysis of the material was made to ascertain functional group presence in the unheated material, the results of which are presented in Fig. 1 and Table I.

Fig. 1

Infrared Spectrum of CATCP (3-3-I)

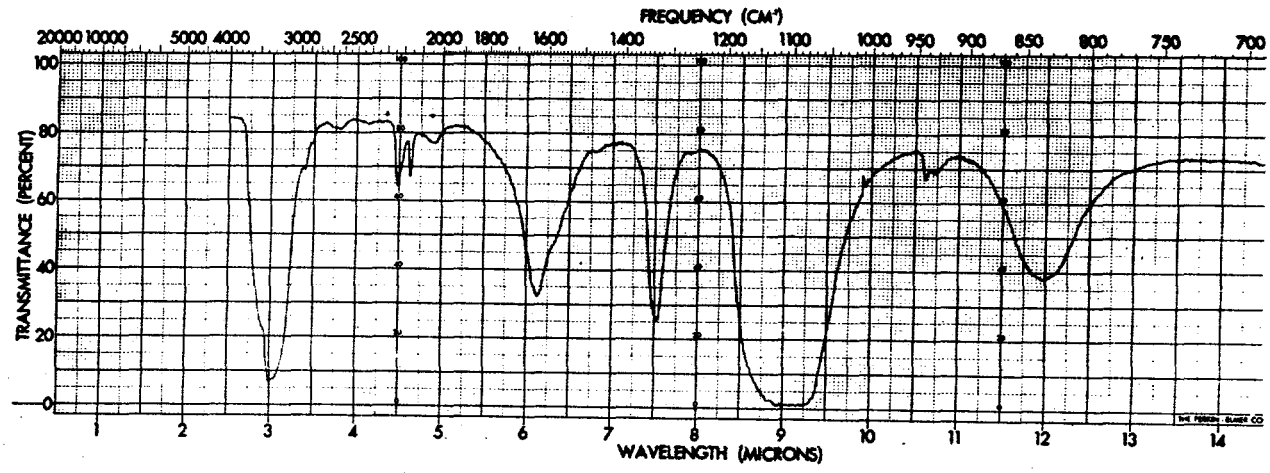


Table I

Infrared Band Assignments for CATCP (3-3-I)

μ	Functional Group	Mode
2.90	O-H	ν_s
3.0-3.2	N-H	ν_{a+s}
4.49	C≡N (bridged)†	ν_s
4.63	C≡N (terminal)	ν_s
6.15	O-H	δ_d
	N-H	δ_d
7.55	NH_3 (coordinated)	δ_s
8.8-9.3	ClO_4^-	ν_d
10.60	ClO_4^-	ν_s
10.70	H_2O (coordinated)	ρ_r
11.90	NH_3 (coordinated)	ρ_r

†*K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley (1963) P 172.*

Chemical analysis of the material (and all subsequent thermally treated samples) was restricted to carbon, hydrogen, and nitrogen analysis (Table II).

Table II

Carbon, Hydrogen, and Nitrogen Analysis of CATCP (3-3-I)
(Weight %)

	Carbon	Hydrogen	Nitrogen
	3.09	4.02	18.08
	3.08	4.01	18.12
	3.07	3.98	18.11
	3.08	4.00	18.09
Average	3.08	4.00	18.10

Based upon these data and in consideration of functional group presence (Fig. 1, Table I), the following results are obtained with respect to a molar ratio of $CN/NH_3/H_2O$:

$$C_{3.08} \qquad N_{18.10} \qquad H_{4.00}$$

$$C_{1.0} \qquad N_{5.04} \qquad H_{15.48}$$

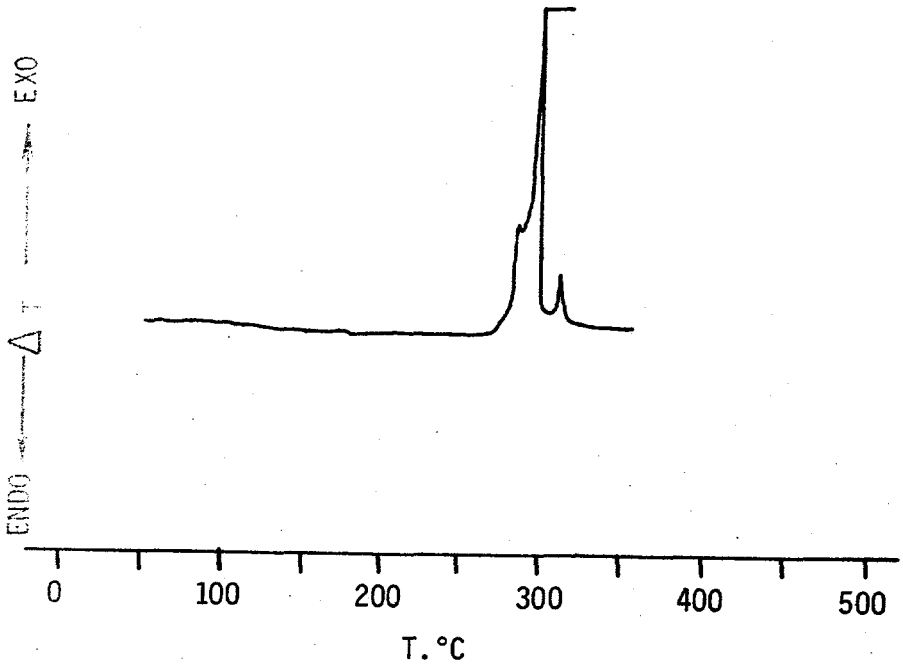
$$(CN)/(NH_3)/(H_2O) = 1.0/4.04/1.68$$

These results show a very close adherence to the stoichiometric ratio for the tetrammine cyano grouping. At least one water of coordination is indicated; however, the excess (1.68/1.00) could possibly be attributed to the presence of some di aquo or some interstitial moisture, or both.

The results of differential thermal analysis (DTA) indicates a minor endotherm at 180°C with the exotherm threshold at approximately 270°C (Fig. 2).

Fig. 2

DTA Thermogram of CATCP (3-3-I)
(20°C/min)



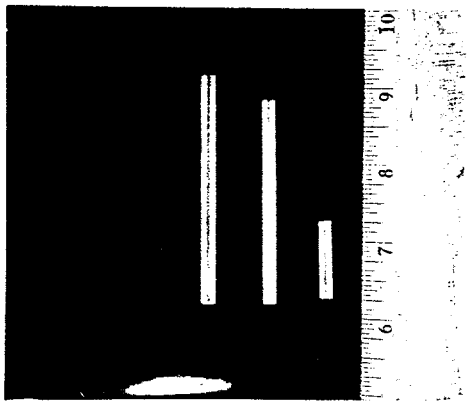


Fig. 3

Aluminum Sample Configurations

The physicochemical investigation of the unheated material fundamentally involved its storage in uniform system configurations under specifically chosen thermal conditions with system variables including time, sample geometry, and physical restrictions (open and closed systems).

The physical aspects of the study included photomicrography, specific surface area determination (gas adsorptometry), spark sensitivity, and crystal density measurement (x-ray diffraction).

Thermal Study Considerations

Preliminary studies of the CATCP (3-3-I) involved the determination of impact sensitivity (drop hammer) and the electrostatic sensitivity (spark gap). The results obtained were as follows:

Impact Sensitivity (12 A, sandpaper)	37 cm, σ = 0.03
Impact Sensitivity (12 B, steel)	25 cm, σ = 0.05
Spark Sensitivity (5 kV)	0.15 mfd

After drying the unheated material (3-3-I) over a desiccant (H_2SO_4) for 24 hours, the study was systemized by placing a weighed amount in aluminum sample configurations (Fig. 3).

These sample configurations, as seen in Fig. 3, consisted of (left to right) a unibody right circular cylinder closed at one end, while the remaining items are solid right circular cylinders whose diameters match the inside diameter of the former, so as to produce a nearly perfect closed system when the 'plug' is set in place by means of a small pellet press. The longer of the two plugs is

of such a length so as to produce a sample density of 0.85 gm/cc, while the shorter is for maintaining a closed system at bulk density. After the material was weighed and placed in the aluminum cylinders they were modified so as to produce four system configurations;

1. Open bulk
2. Closed bulk
3. Open compact[1]
4. Closed compact

The completed configurations were placed in analytical ovens maintained at specific temperatures for extended periods of time, divided into the following groups:

Thermal Group I (70°C, 20 hours @ 570 mm)

Thermal Group II (100°C, 20 hours, atmospheric pressure)

Thermal Group III (120°C, 20 hours, atmospheric pressure)

Thermal Group IV (120°C, 100 hours, atmospheric pressure)

Thermal Group V (100°C, open bulk, 1-336 hours, atmospheric pressure)

Thermal Group VI (120°C, open bulk, 1-336 hours, atmospheric pressure)

At the completion of the thermal conditioning of each sample set, evaluation of the material was made from data obtained through the following procedures:

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[1]*This system is obtained by removal of the closure plug after attaining a sample density of 0.85 gm/cc.*

1. Infrared spectral analysis
2. Carbon, hydrogen, and nitrogen analysis
3. Differential thermal analysis
4. X-ray diffraction
5. Surface area measurements
6. Photomicrography

Thin layer chromatography studies were not made on the thermal residues since no solvent has yet been found. The heated material does 'dissolve' in ethylenediamine; however, it does not undergo solvation but rather is converted to an ethylenediamine complex.

Experimental

Thermal Group I (70°C, 20 hours @ 570 mm) - Results are given in Table III.

Table III

Results - Thermal Group I

Temperature (°C): 70 Time (hrs.): 20 Pressure: 570 mm (Hg)

	System Configuration				
	Original Bulk	Open Bulk	Closed Bulk	Open Compact	Closed Compact
Carbon (%)	3.08	3.06	3.12	3.04	3.06
Nitrogen (%)	18.10	17.97	18.15	17.87	17.98
Hydrogen (%)	4.00	3.82	3.85	3.88	3.74
Weight Loss (%)	0.00	1.94	0.64	2.04	0.60
C/N Ratio	1.0/5.04	1.0/5.04	1.0/4.99	1.0/5.04	1.0/5.04
Surface Area (m^2/gm)	25.5	21.2	22.9	21.9	24.1
Infrared Spectra, Fig. No.	1	4(a)	4(b)	4(c)	4(d)
DTA, Fig. No.	2	5(a)	5(b)	5(c)	5(d)
Photomicrograph, Fig. No.	8	8	8	8	8

Infrared spectral analysis indicates no detectable change in the molecular (functional group) composition under these specific thermal-time conditions as a function of system configuration. There is no indication of further bridging of the cyano group (C≡N) at 4.49 and 4.63 μ [Fig. 4(a)][2]. The weight loss data (Table III), when considered with the foregoing indications, imply only water

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[2] *It can be seen in the majority of spectra presented in this report that the absorption band due to the perchlorate (ClO_4^-, ~ 8.8-9.3 μ) is not resolved as the concentration in the KBr pellets was increased so as to enhance the definition of absorption bands of other functional groups.*

loss, which if resulting substantially from coordinated water, is only partial and does not seem to indicate further bridging of the cyano group as experienced at higher temperatures (100°, 120°C). This could be attributed to too low a temperature-time composite relative to threshold. The variation in the amount of weight loss can be seen to relate to system configuration, the greatest losses experienced by the open system configurations (Figs. 6 and 7).

Differential thermal analysis indicates a change in the material as a function of system configuration by the change in the character and position of the endotherm at ∿ 100°C, most pronounced in the closed compacted system which may be related to its undergoing the least weight loss and the least change in particle surface area of the four configurations [Figs. 2, 5(a,b,c,d)].

X-ray diffraction studies of the thermal residues only indicate some slight change in the crystal structure between the residues and the original unheated material, but no detectable differences among the four configuration residues.

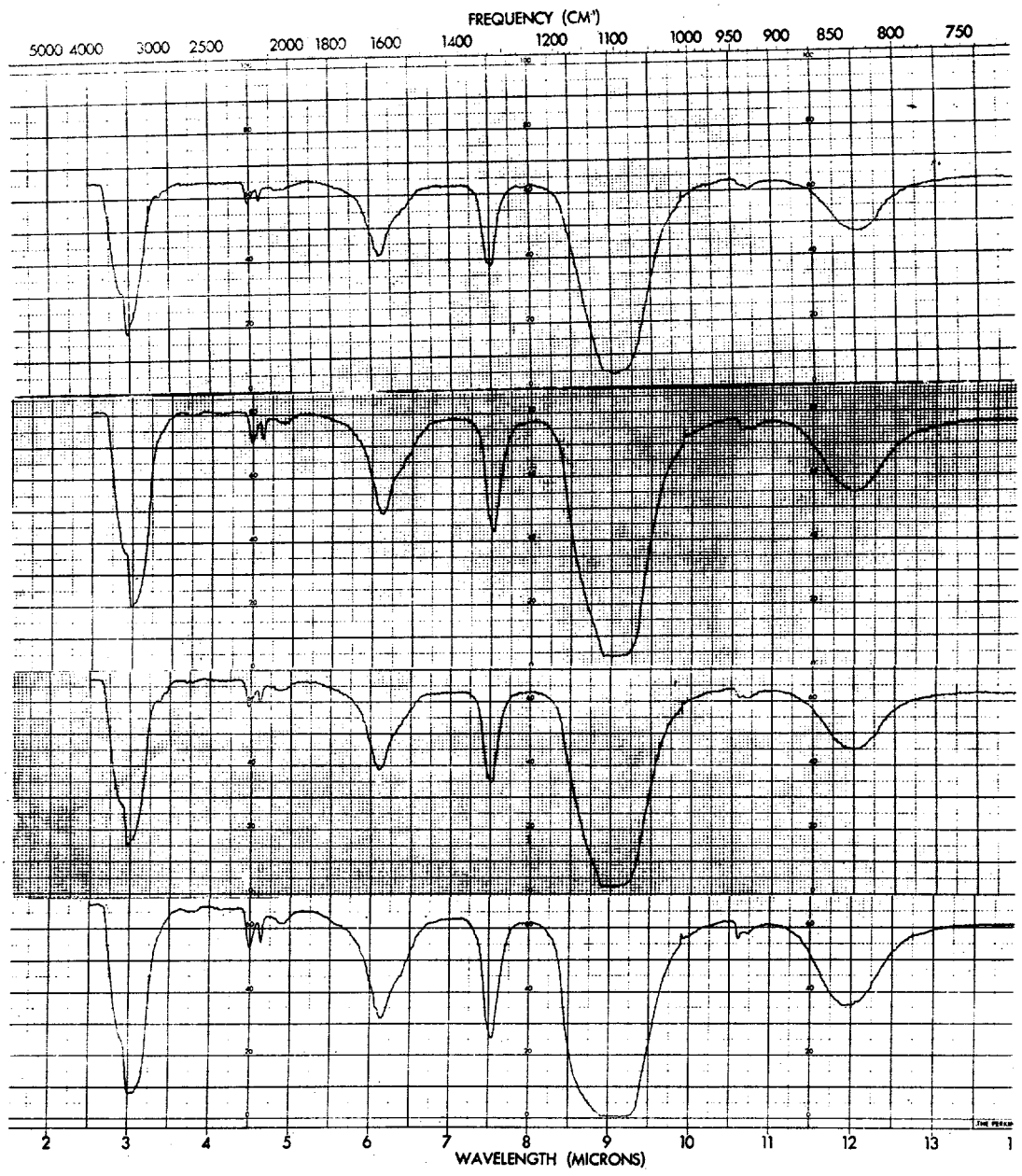
Surface area measurements (gas adsorptometry) do show a possible relationship between the time-weight loss data and the surface area change, the latter following a decreasing pattern under this particular set of thermal conditions (Fig. 8). The relative effect of storage at reduced pressure (570 mm) can only be conjective, as this set of conditions was unique to this particular sample set as all other sets were thermally treated at atmospheric pressure, ∿ 675 mm.

Photomicrographs of the thermal residues show decreases in particle size, the more pronounced exhibited in the open and closed compacted configurations (Fig. 8).

This decrease was not due solely to the physical (mechanical) compression prior to the thermal aging as can be seen from the photomicrograph of the original unheated closed compacted material (Fig. 37).

Fig. 4

Infrared Spectra of CATCP Residues
[70 C, 20 hrs. @ 570 mm (Hg)]



(a) open bulk

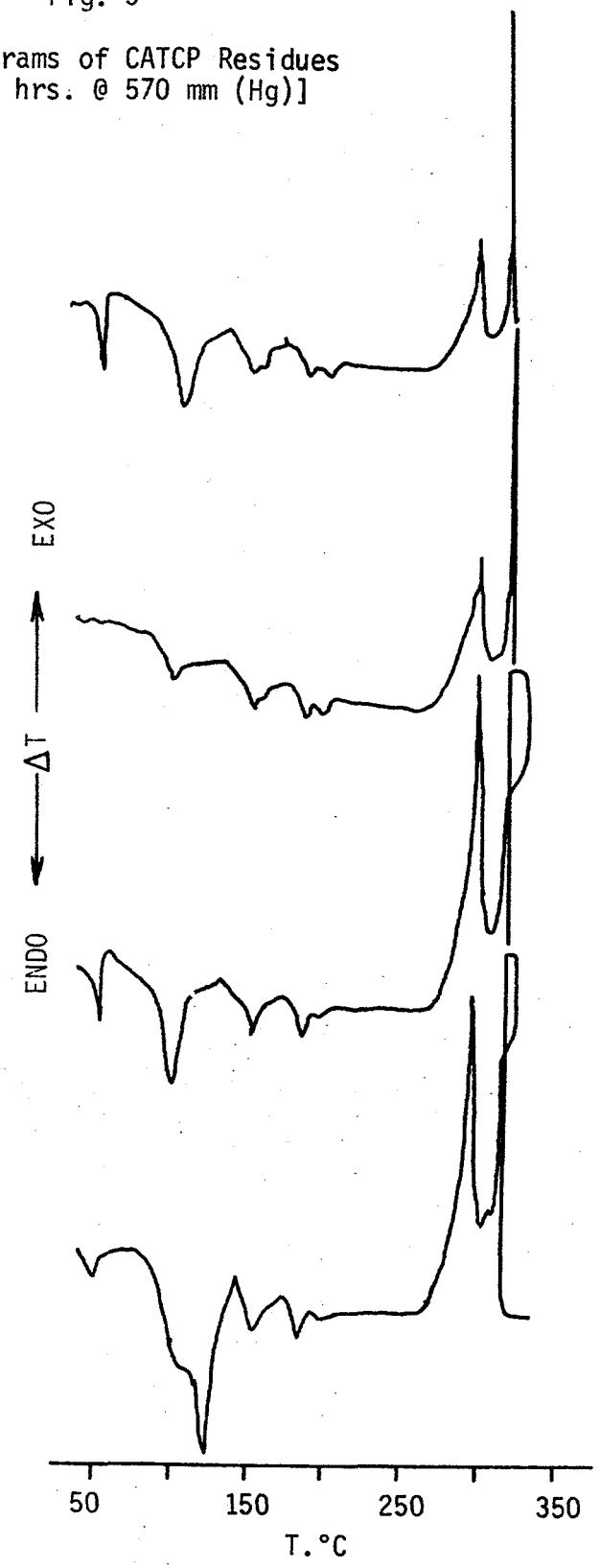
(b) closed bulk

(c) open compact

(d) closed compact

Fig. 5

DTA Thermograms of CATCP Residues
[70°C, 20 hrs. @ 570 mm (Hg)]



(a) open bulk

(b) closed bulk

(c) open compact

(d) closed compact

Fig. 6

CATCP 3-3-I
Weight loss with time
[70°C, 20 hrs. @ 570 mm (Hg)]

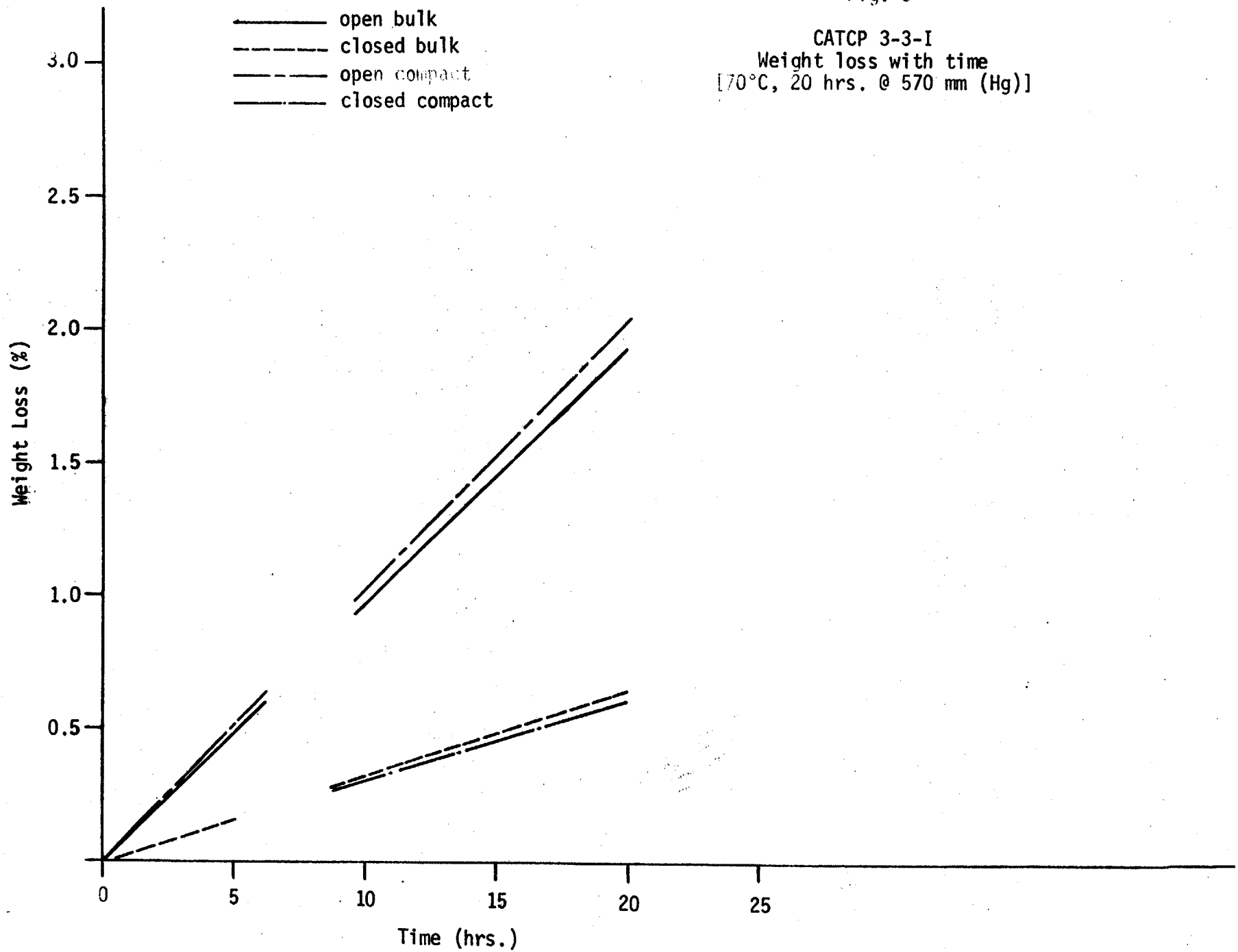
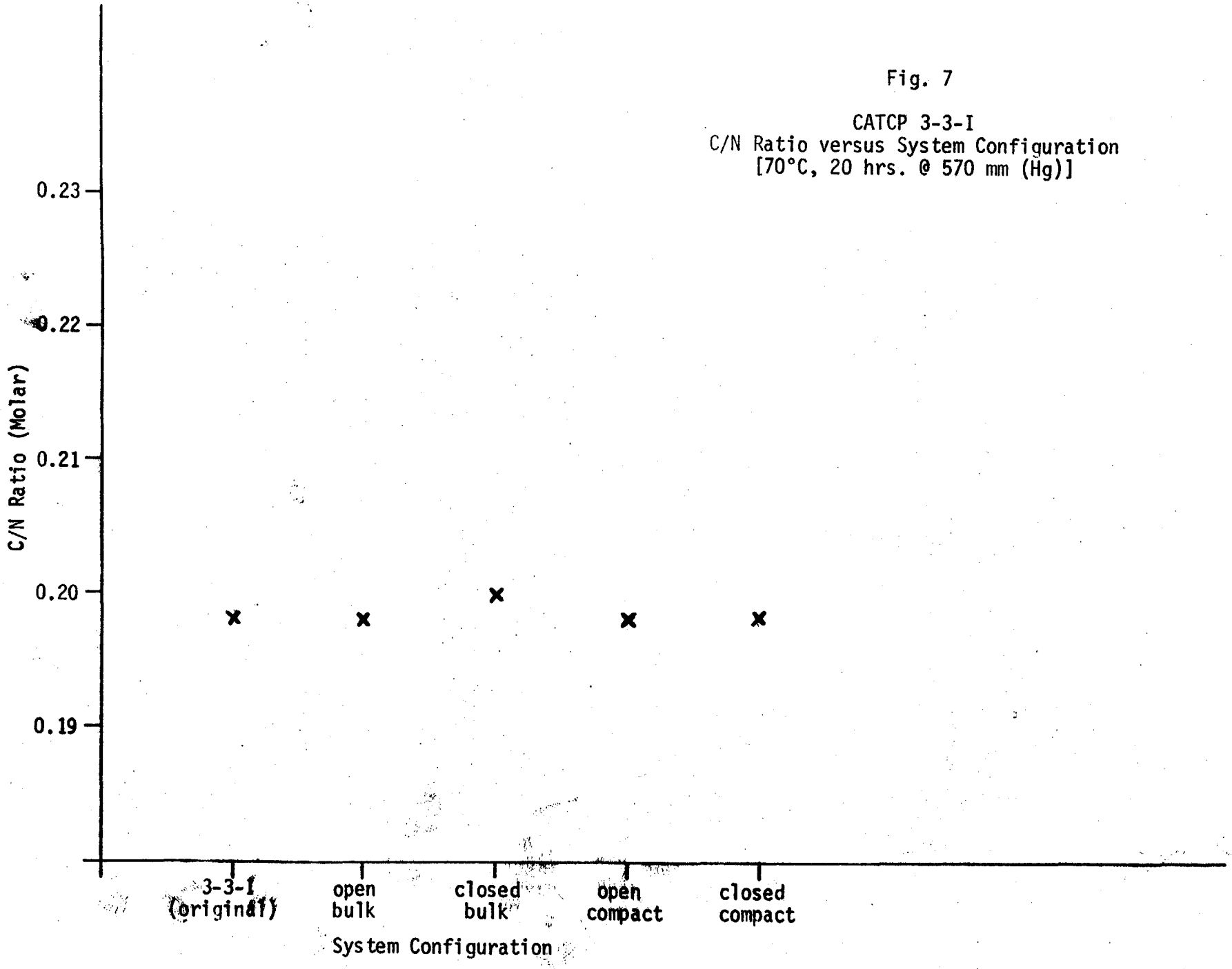


Fig. 7

CATCP 3-3-I
C/N Ratio versus System Configuration
[70°C, 20 hrs. @ 570 mm (Hg)]



Original

Open Bulk

Closed Bulk

Open Compact

Closed Compact

Fig. 8

Photomicrographs of CATCP 3-3-I Residues (X925)
[70°C, 20 hrs. @ 570 mm (Hg)]

Thermal Group II (100°C, 20 hours) - Results are given in Table IV.

Table IV

Results - Thermal Group II

Temperature (°C): 100 Time (hrs.): 20 Pressure: Atmospheric

	System Configuration				
	Original Bulk	Open Bulk	Closed Bulk	Open Compact	Closed Compact
Carbon (%)	3.08	3.05	3.06	3.17	3.16
Nitrogen (%)	18.10	17.83	18.00	18.19	18.02
Hydrogen (%)	4.00	3.78	3.79	3.75	3.83
Weight Loss (%)	0.00	2.81	1.69	2.93	1.45
C/N Ratio	1.0/5.04	1.0/5.01	1.0/5.04	1.0/4.92	1.0/4.89
Surface Area (m^2/gm)	25.5	20.9	23.9	23.9	20.6
Infrared Spectra, Fig. No.	1	9(a)	9(b)	9(c)	9(d)
DTA, Fig. No.	2	10(a)	10(b)	10(c)	10(d)
Photomicrograph, Fig. No.	13	13	13	13	13

Infrared spectral analyses of these residues [Fig. 1, 9(a-d)] do not indicate an appreciable further bridging of the cyano group (4.49 and 4.63 μ) under these conditions of the thermal-time composite. However, there is a slight indication of the formation of an ammonium product(s) ($:NH_3 \rightarrow NH_4$) which seems to be a result of sample storage in the open bulk and open compact configurations only ($\sim$ 6.85-7.00 μ, δ_d). Neither closed system indicates this change. Additionally there is an indication of decreased aquation (coordinated) of the material creating a molecular (structural) change which would dampen the observed rocking mode

of ligand water ($:OH_2$) at 10.70 μ (ρ_r). This characteristic appears to occur with the open bulk and open compact systems which undergo the more substantial weight loss during thermal aging (Table IV, Fig. 11).

Chemical analyses do indicate a slight loss of coordinated ammonia ($:NH_3$). This is predicated on the nature of the cyano group ($C\equiv N$) which when ionicly bonded to a ligand orbital position is more stable than nitrogen lone-pair species even when in a bridged configuration. Accordingly, the loss could be attributed to the ammine ligand (Fig. 12). The greatest increase in the molar C/N ratio can be seen in the compacted systems, both open and closed (Table IV, Fig. 12). These results indicate the reaction threshold for this occurrence is apparently decreased by the relative restriction of the material in its compacted configuration.

Differential thermal analyses show the least change occurring in the open and closed bulk systems, with the open and closed compacted systems undergoing a substantial transition. This is particularly noticeable in regards to the endothermic nature of the closed compacted sample in the range of 180 to 190°C, and in the change in the exothermic character at 275 to 320°C [Figs. 2, 10(a-d)].

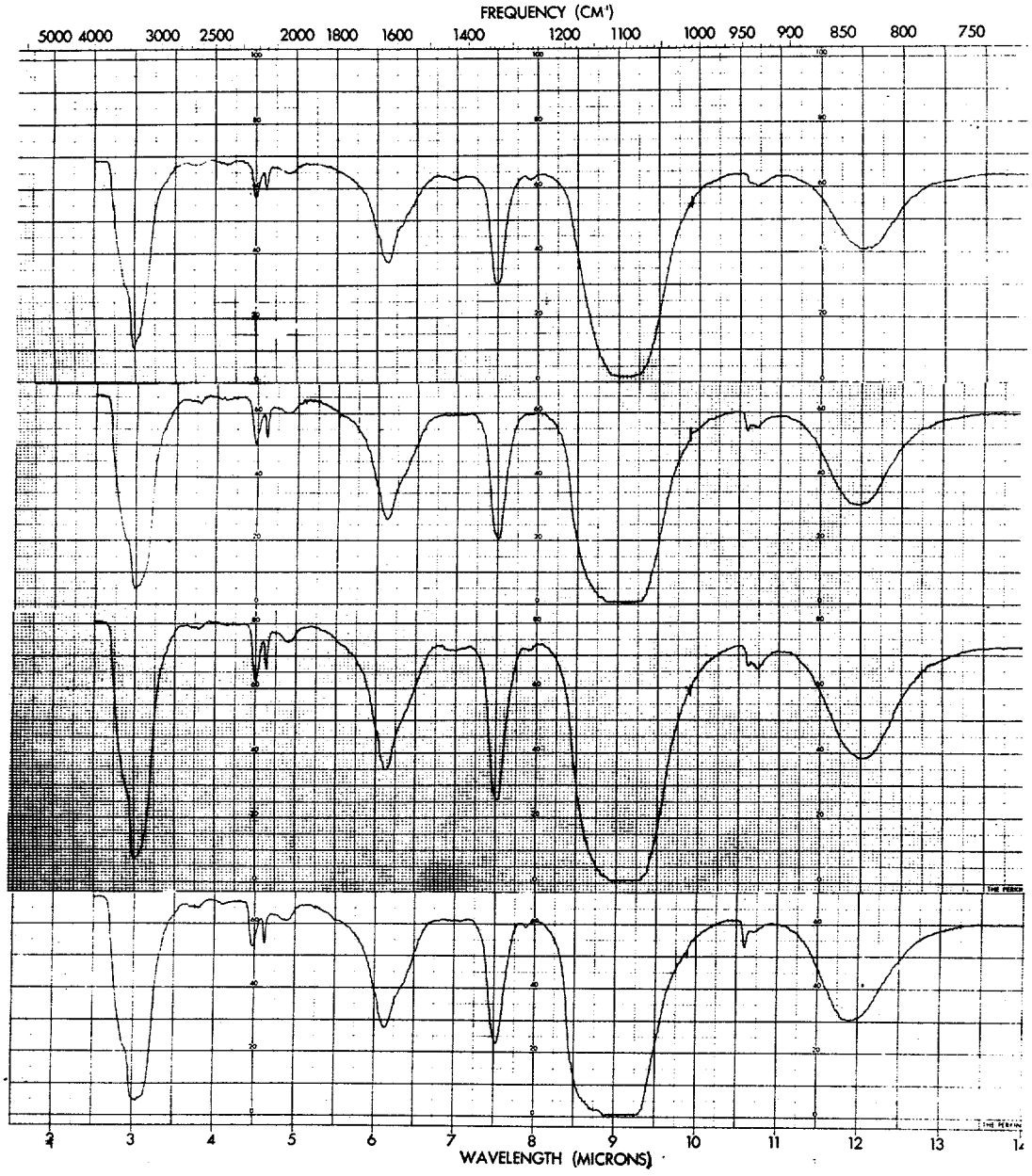
X-ray diffraction studies do not indicate a structural change in the residues, probably due to an insufficient percentage change in the sample to be diffraction sensitive.

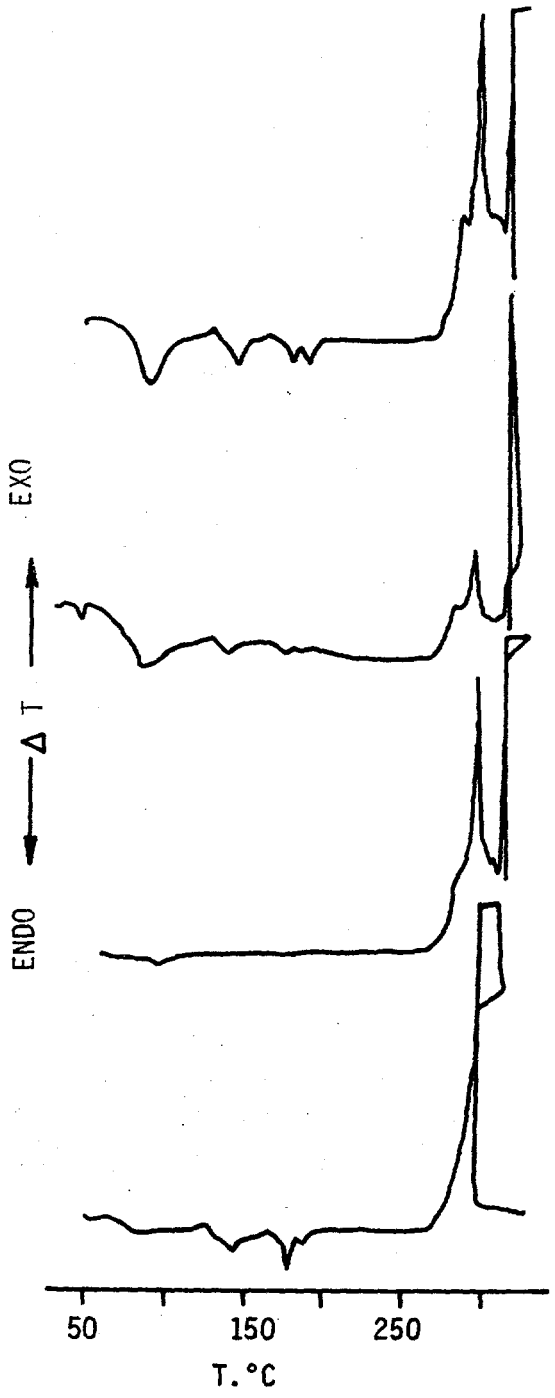
Surface area measurements (gas adsorptometry) show an anomaly in that no relationship is apparent between weight loss and change in surface area (ΔS_o). ΔS_o is

greatest in the closed compacted system; however, approximately the same change is seen with the open bulk residues (Table IV). Photomicrographs of the residues would indicate this occurrence may be due to an appreciably larger cavitation effect occurring in the open bulk configuration (Fig. 13).

Fig. 9

Infrared Spectra of CATCP Residues
(100°C, 20 hrs.)





(a) open bulk

(b) closed bulk

(c) open compact

(d) closed compact

Fig. 10

DTA Thermograms of CATCP Residues
(100°C, 20 hrs.)

Fig. 11

CATCP 3-3-I
Weight loss with time
(100°C, 20 hrs.)

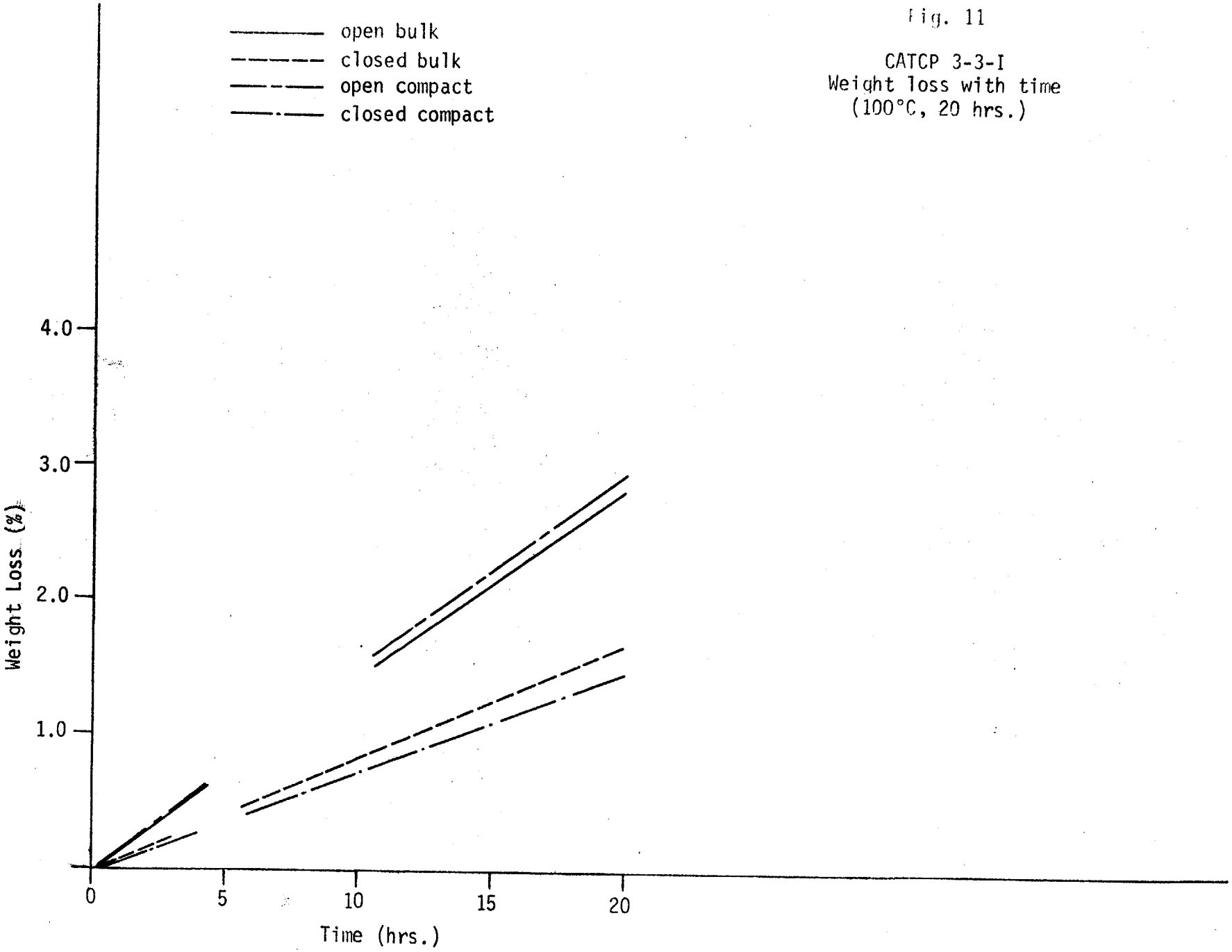
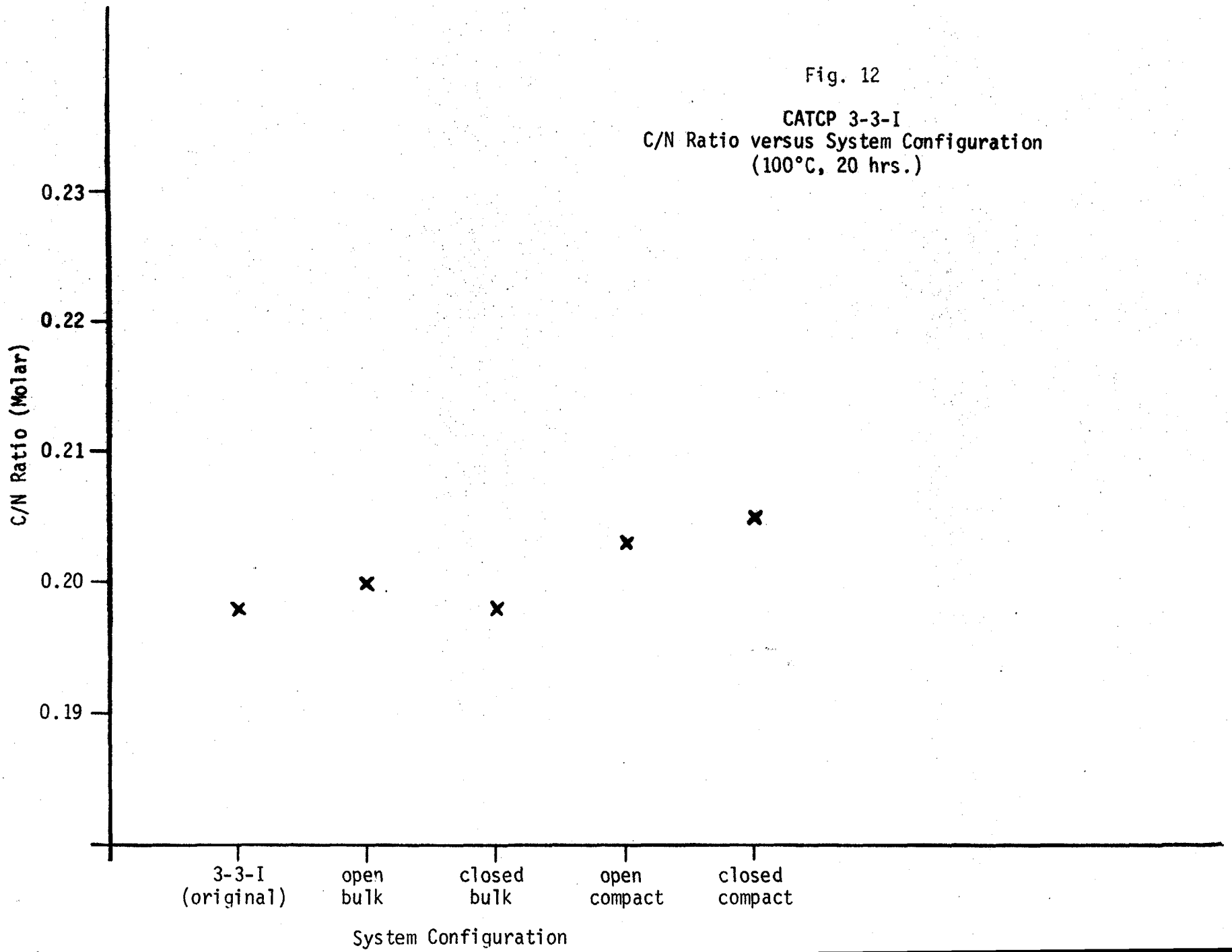


Fig. 12

CATCP 3-3-I
C/N Ratio versus System Configuration
(100°C, 20 hrs.)



Original

Open Bulk

Closed Bulk

Open Compact

Closed Compact

Fig. 13

Photomicrographs of CATCP 3-3-I Residues (X925)
(100°C for 20 hrs.)

Thermal Group III (120°C, 20 hours) - Results are given in Table V.

Table V

Results - Thermal Group III

Temperature (°C): 120 Time (hrs.): 20 Pressure: Atmospheric

	System Configuration				
	Original Bulk	Open Bulk	Closed Bulk	Open Compact	Closed Compact
Carbon (%)	3.08	3.12	3.09	3.49	3.03
Nitrogen (%)	18.10	18.65	17.96	18.70	17.75
Hydrogen (%)	4.00	3.40	3.56	3.49	3.62
Weight Loss (%)	0.00	6.66	2.54	6.31	2.43
C/N Ratio	1.0/5.04	1.0/5.12	1.0/4.98	1.0/4.60	1.0/5.02
Surface Area (m^2/gm)	25.5	36.2	23.9	37.4	23.5
Infrared Spectra, Fig. No.	1	14(a)	14(b)	14(c)	14(d)
DTA, Fig. No.	2	15(a)	15(b)	15(c)	15(d)
Photomicrograph, Fig. No.	17	17	17	17	17

Infrared spectral analyses of the thermal residues from this group indicate a consistency experienced in earlier thermal studies of the precursors of CATCP 3-3-I [Figs. 1, 14(a-d)]. The thermal treatment of CATCP materials, at or above the kinetic threshold for cyano bridging, has consistently resulted in the apparent total bridging of the cyano group in the open bulk and open compacted configurations. This conversion did not occur in either closed configurations, even at 120°C after 336 hours (Fig. 33). The absorption band at 4.49 μ is assigned to the symmetric stretching mode of the cyano group when in the bridged configuration (:N≡C-, ν_s) and this effect of total and partial bridging can be seen in Fig. 14,

spectra a and c and spectra b and d, respectively.[3] The absorption band due to coordinated water (:OH_2, ρ_r, 10.7 μ) indicates a relationship to the cyano bridging conversion by the decrease in the band intensity at this wavelength, characteristic of loss of coordinated water. It has been assumed that the prerequisite for the cyano bridging mechanism is this loss of coordinated water from the coordination sphere. The increased presence of an ammonium product(s), which was indicated in the study of the Thermal Group II residues, is not apparent and is probably due to sublimation of the materials in the open configurations at this increased kinetic level. A sublimation study of CATCP (3-3-I) carried out at 120°C for 30 hours did result in a small deposit of ammonium perchlorate on the system condensing device (cold finger).

Chemical analyses of the residues indicate a loss of coordinated ammonia as the C/N molar ratio increases for the open compacted sample (1.0/5.04 → 1.0/4.60), and infrared spectral analyses indicate an increased amount of water (2.9 μ), conceivably taking up the orbital ligand position vacated by ejected ligand ammonia [Table V, Fig. 14(c) and Fig. 16].

Differential thermal analyses point up this open system consistency by the substantial presence of the 45°C and the 100 to 145°C endotherms, found only in the open configuration residues (bulk and compact) [Figs. 2, 15(a-d)].

X-ray diffraction studies indicate a structural change for both the open bulk and open compact, but diffraction patterns obtained for the closed bulk and closed compact residues have not changed from those obtained from the Thermal Group II residues.

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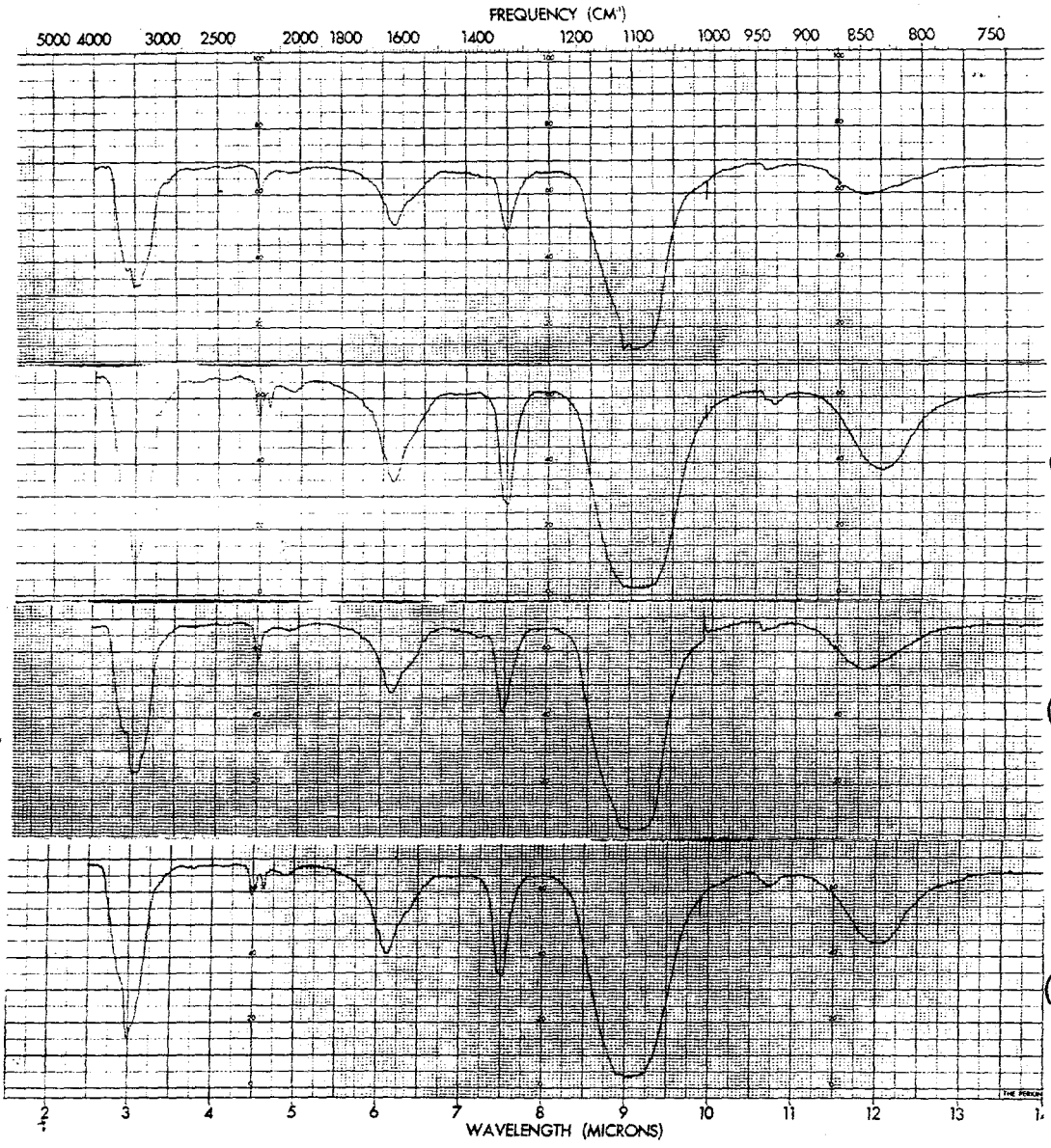
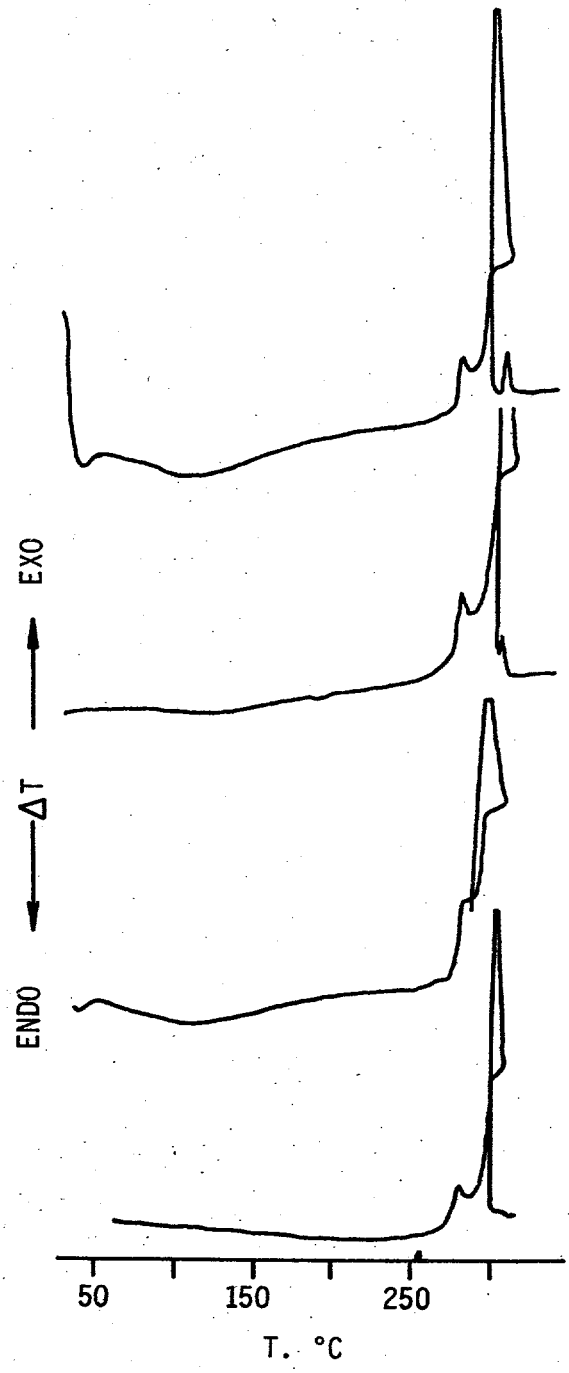
[3] *K. Nakomoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley (1963) p. 166.*

Surface area measurements (Table V) follow the conversion consistency in that both open bulk and open compact show a substantial increase (+42 and +46%, respectively) while the closed bulk and closed compact show a decrease as previously experienced when total cyano bridging conversion was not effected (-6.3 and -7.8%, respectively). Photomicrographs (Fig. 17) of the residues show a change in crystal size and shape for both the converted materials (open bulk and open compact) while the closed configuration samples show relatively the same particle shape as the unheated material but with some size change. Since the surface area has decreased, this would indicate a decrease in the cavitation effect.

Fig. 14

Infrared Spectra of CATCP Residues
(120°C, 20 hrs.)





(a) open bulk

(b) closed bulk

(c) open compact

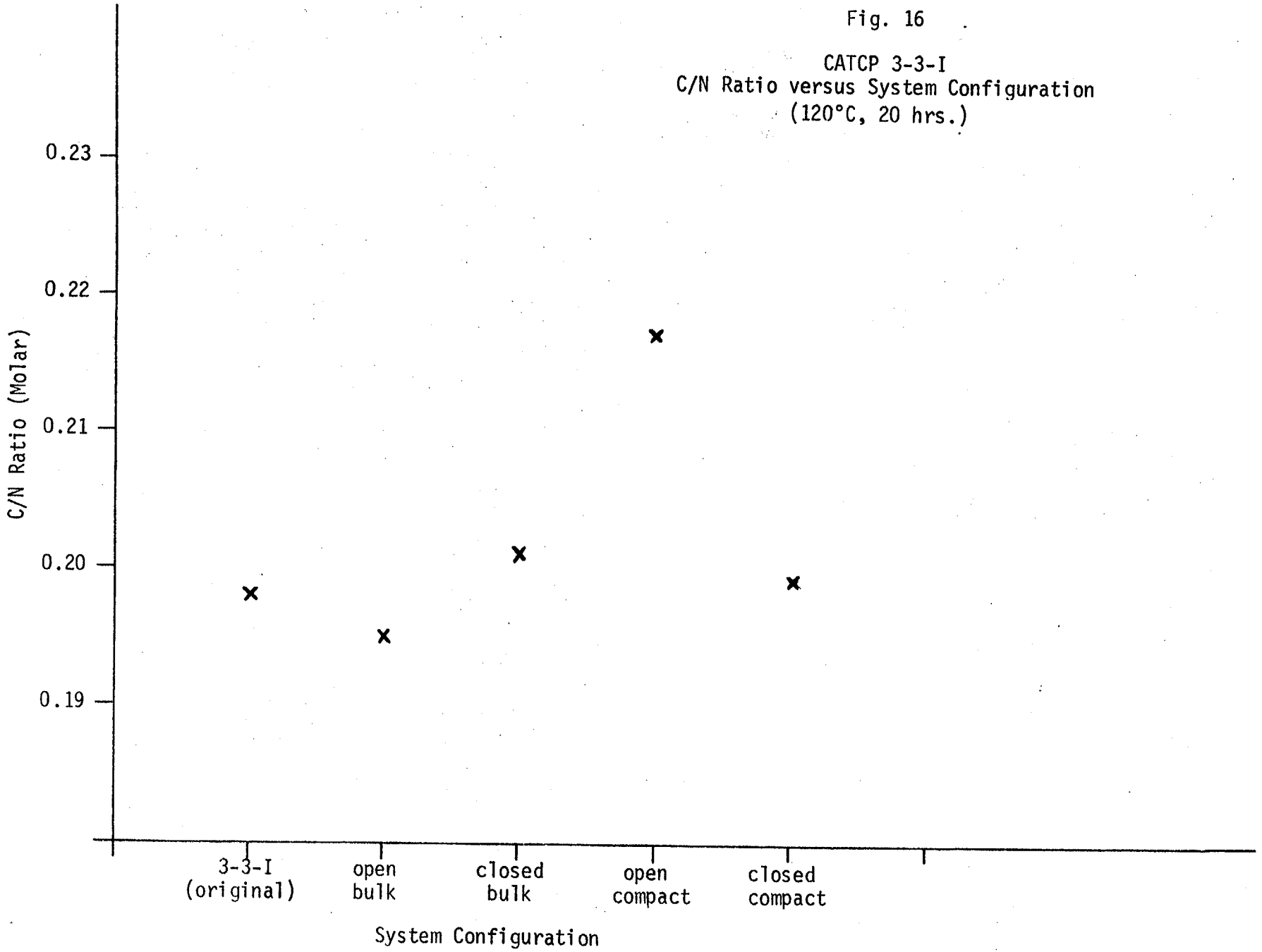
(d) closed compact

Fig. 15

DTA Thermograms of CATCP Residues
(120°C, 20 hrs.)

Fig. 16

CATCP 3-3-I
C/N Ratio versus System Configuration
(120°C, 20 hrs.)



Original

Open Bulk

Closed Bulk

Open Compact

Closed Compact

Fig. 17

Photomicrographs of CATCP 3-3-I Residues (X925)
(120°C for 20 hrs.)

Thermal Group IV (120°C, 100 hours) - Results are given in Table VI.

Table VI

Results - Thermal Group IV

Temperature (°C): 120 Time (hrs.): 100 Pressure: Atmospheric

	System Configuration				
	Original Bulk	Open Bulk	Closed Bulk	Open Compact	Closed Compact
Carbon (%)	3.08	3.12	3.09	3.49	3.03
Nitrogen (%)	18.10	18.78	18.09	18.84	17.88
Hydrogen (%)	4.00	3.38	3.54	3.47	3.59
Weight Loss (%)	0.00	7.01	2.83	6.65	2.80
C/N Ratio	1.0/5.04	1.0/5.16	1.0/5.02	1.0/4.63	1.0/5.06
Surface Area (m^2/gm)	25.5	36.7	19.8	43.6	21.8
Infrared Spectra, Fig. No.	1	18(a)	18(b)	18(c)	18(d)
DTA, Fig. No.	2	19(a)	19(b)	19(c)	19(d)

Infrared spectral analyses of the residues of this group indicate little or no change in the functional group composition of the materials at this temperature (120°C) from samples of similar system configurations as a result of the 80-hour aging extension. The indicated total cyano bridging in the open bulk and open compacted systems as opposed to the non-conversion in the closed bulk and closed compact systems is apparent as seen by the cyano singlet at 4.45 μ in the spectra of the former [Figs. 1, 18(a-d)].

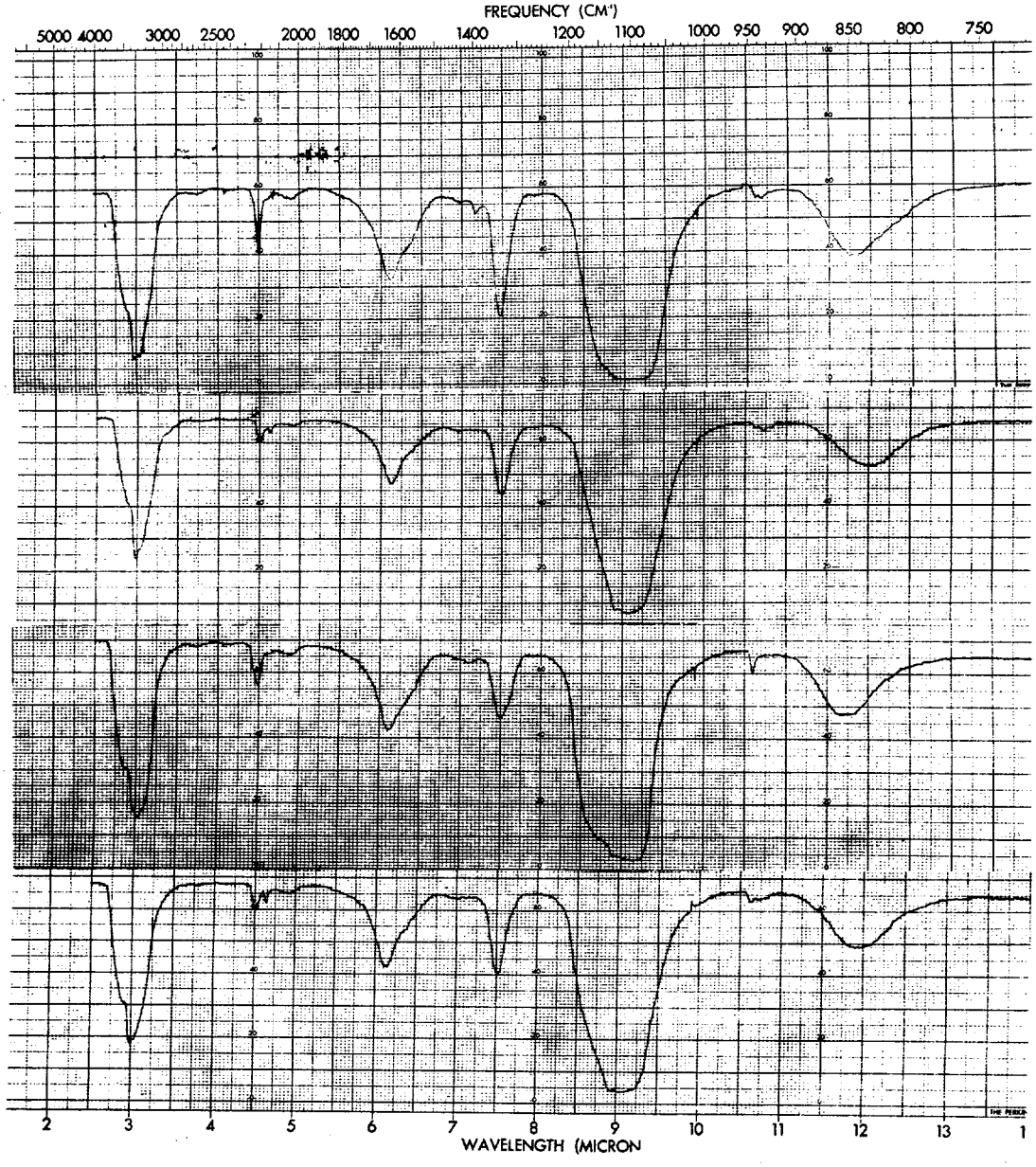
Chemical analyses results, insofar as the molar C/N ratio, would indicate no appreciable chemical change during the 80-hour extension period at 120°C (Table VI, Figs. 20 and 21). Total weight losses increase only slightly during this period.

Differential thermal analyses of the residues do indicate changes during the 80-hour extension, as seen by the loss of the open system endotherms and the change in character of the major exotherms in the region of 270 to 310°C [Figs. 14(a-d), 19(a-d)].

The most prominent feature occurring during the 80-hour extension period is seen in the surface area change of the open compacted sample, where the increase has gone from +46% at 20 hours to +71% at 100 hours (Table VI).

Fig. 18

Infrared Spectra of CATCP Residues
(120°C, 100 hrs.)

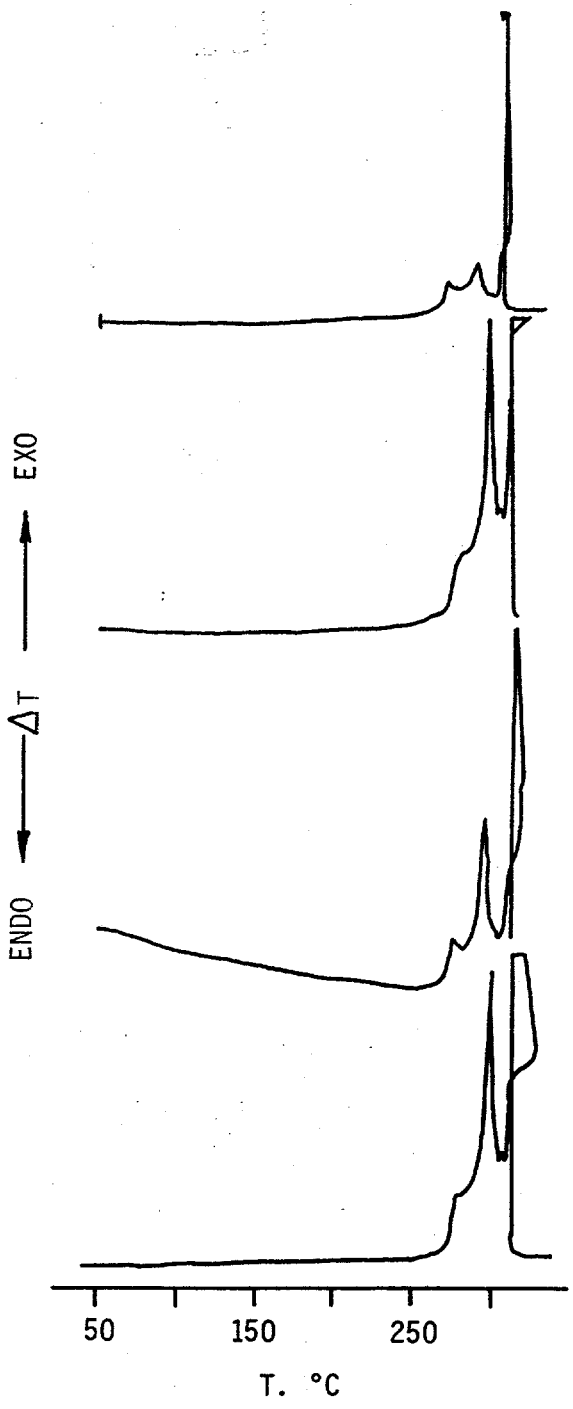


(a) open bulk

(b) closed bulk

(c) open compact

(d) closed compact



(a) open bulk

(b) closed bulk

(c) open compact

(d) closed compact

Fig. 19

DTA Thermograms of CATCP Residues
(120°C, 100 hrs.)

Fig. 20

CATCP 3-3-I
Weight loss with time
(120°C, 100 hrs.)

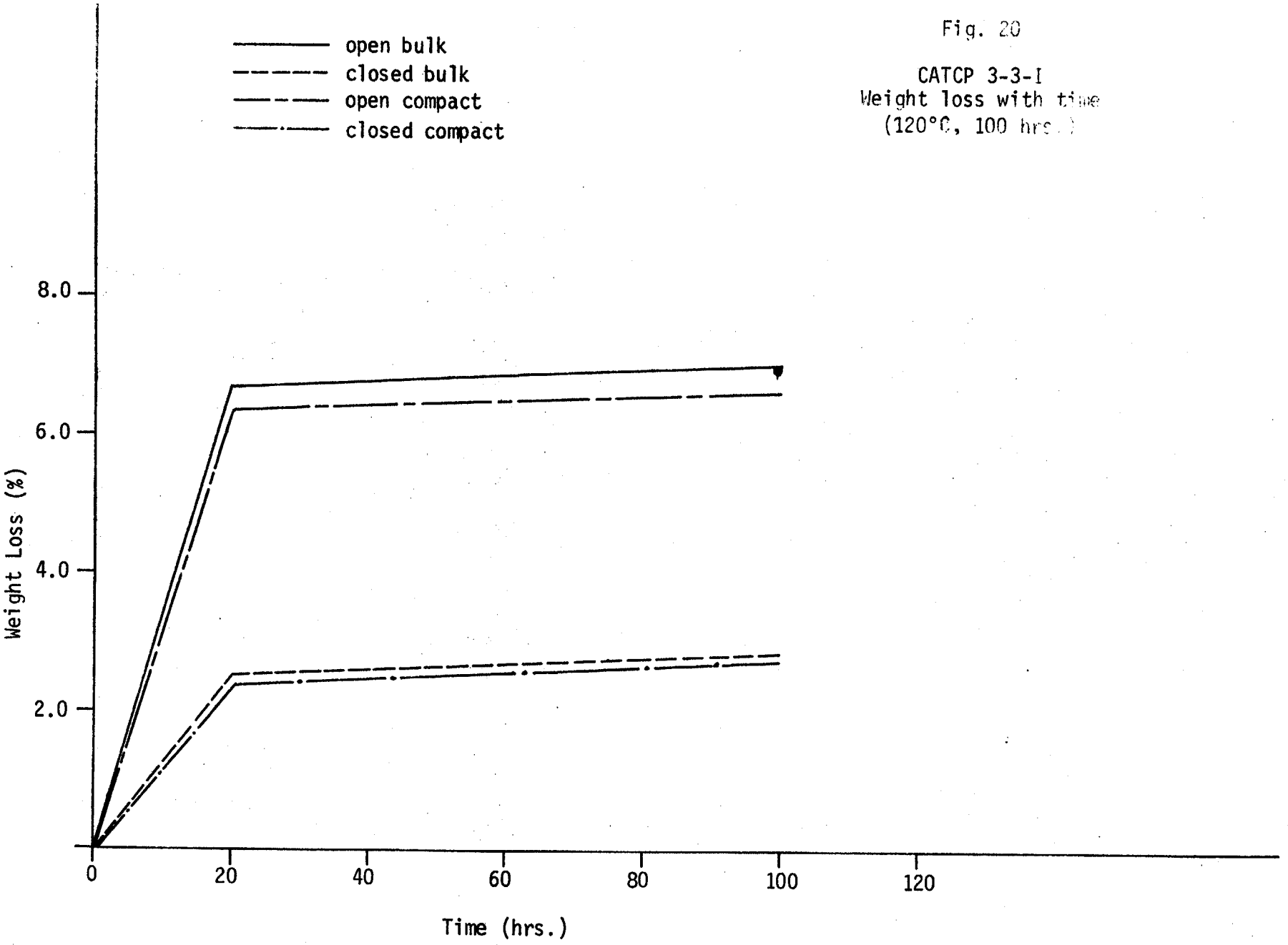
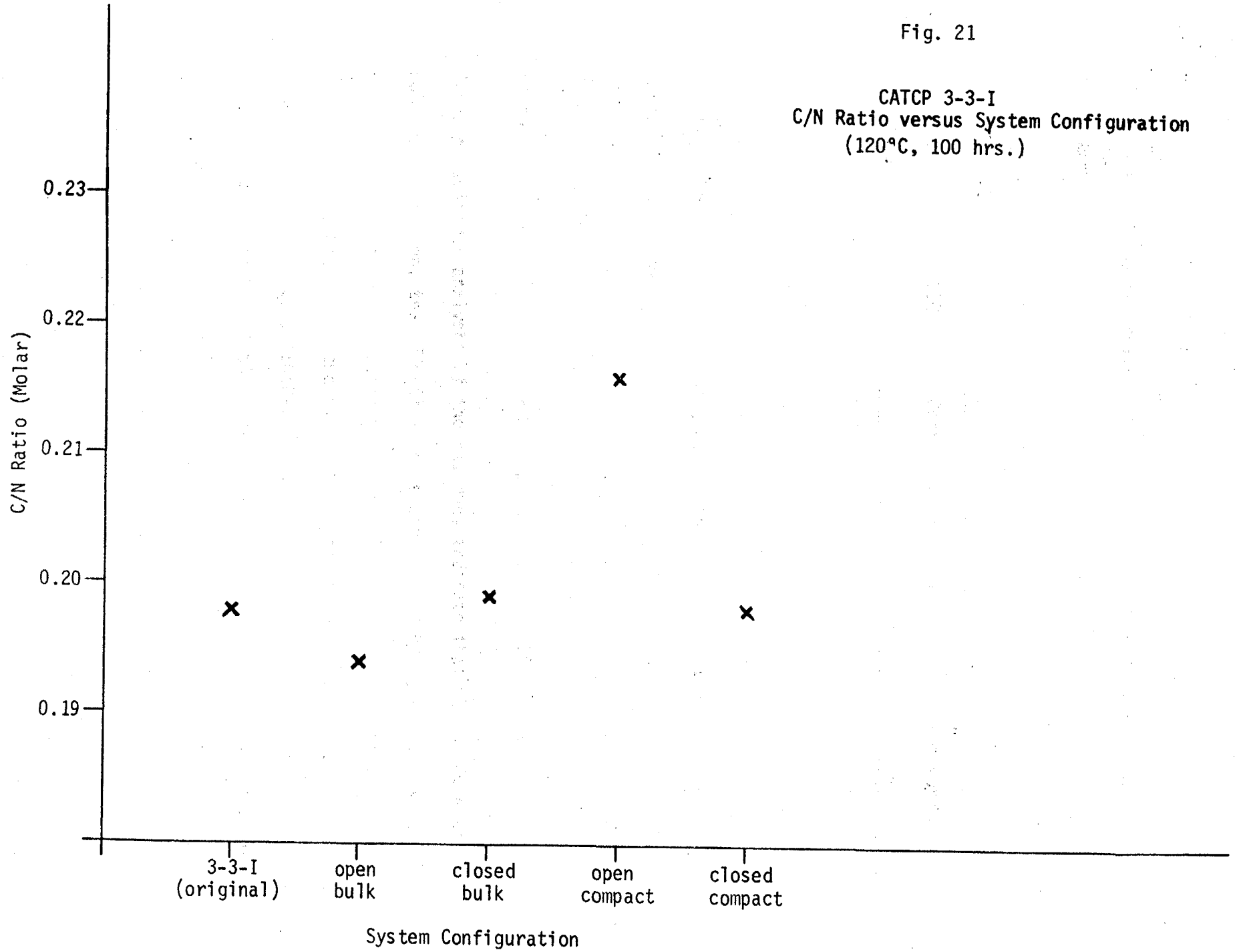


Fig. 21

CATCP 3-3-I
C/N Ratio versus System Configuration
(120°C, 100 hrs.)



Differential thermal analyses of the residues augment this observation by the change in the character of the exothermic group in the region of 280 to 315°C [Fig. 23(a-f)] for the 60-hour results as compared to those obtained for the 24-hour period. Further change in this exothermic pattern is seen at 168 and 336 hours, indications being that little change in structural makeup, if any, occurs after 168 hours.

Chemical analyses show the carbon percentage of the residues to follow a pattern of fluctuation which corresponds to the observed trends seen in the results of infrared and differential thermal analyses (Table VII). The C/N molar ratio reaches a minimum in the 8-hour residue, and between 8 to 24 hours the ratio undergoes a steady increase up to 168 hours, possibly indicative of the nearly complete loss of molecular water during the 8 to 60-hour heating period (Fig. 24).

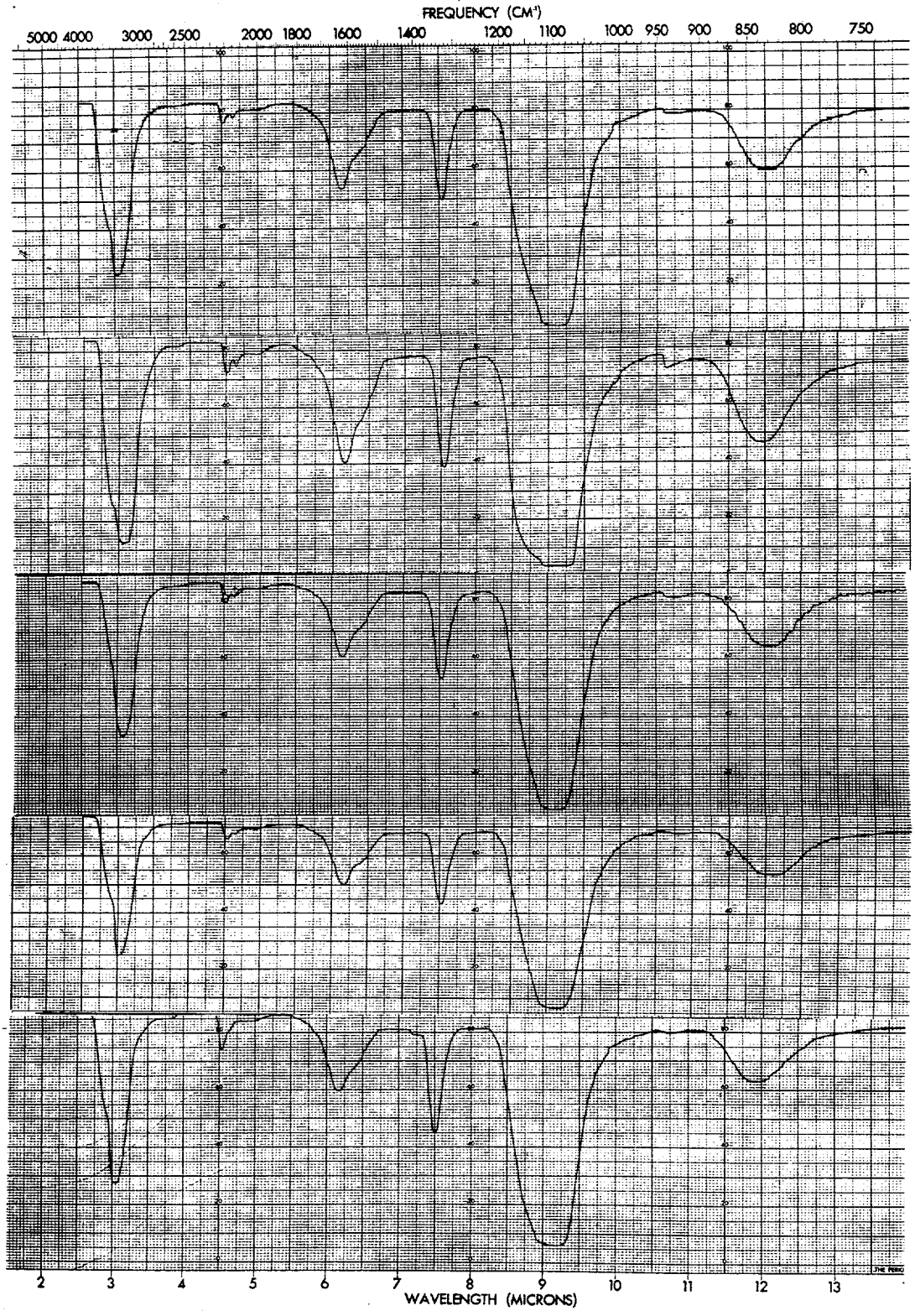
X-ray diffraction analyses indicate a structural change during this period but the resultant patterns are too complex to ascertain an approximate crystal density.

Surface area measurements (gas adsorptometry) show the residues to follow the same pattern of fluctuation, with the maximum decrease occurring near 24 hours followed by a steady increase up to 168 hours with indications of a plateau effect between 168 to 336 hours (Table VII).

Photomicrographs also show an adherence to the fluctuation pattern as seen by the apparent change in particle shape and size from 60 to 168 hours with only a slight change in particle size from 168 to 336 hours (Fig. 25).

Fig. 22

Infrared Spectra of CATCP Residues
(100°C, open bulk)



(a) 1 hr.

(b) 8 hrs.

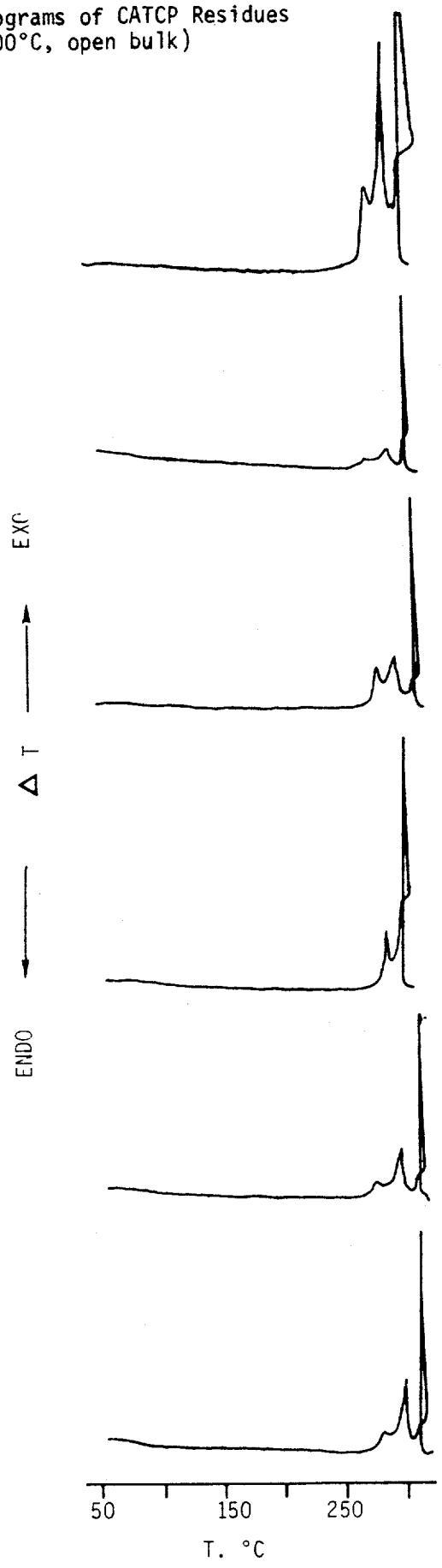
(c) 24 hrs.

(d) 60 hrs.

(e) 168 hrs.

Fig. 23

DTA Thermograms of CATCP Residues
(100°C, open bulk)



(a) 1 hr.

(b) 8 hrs.

(c) 24 hrs.

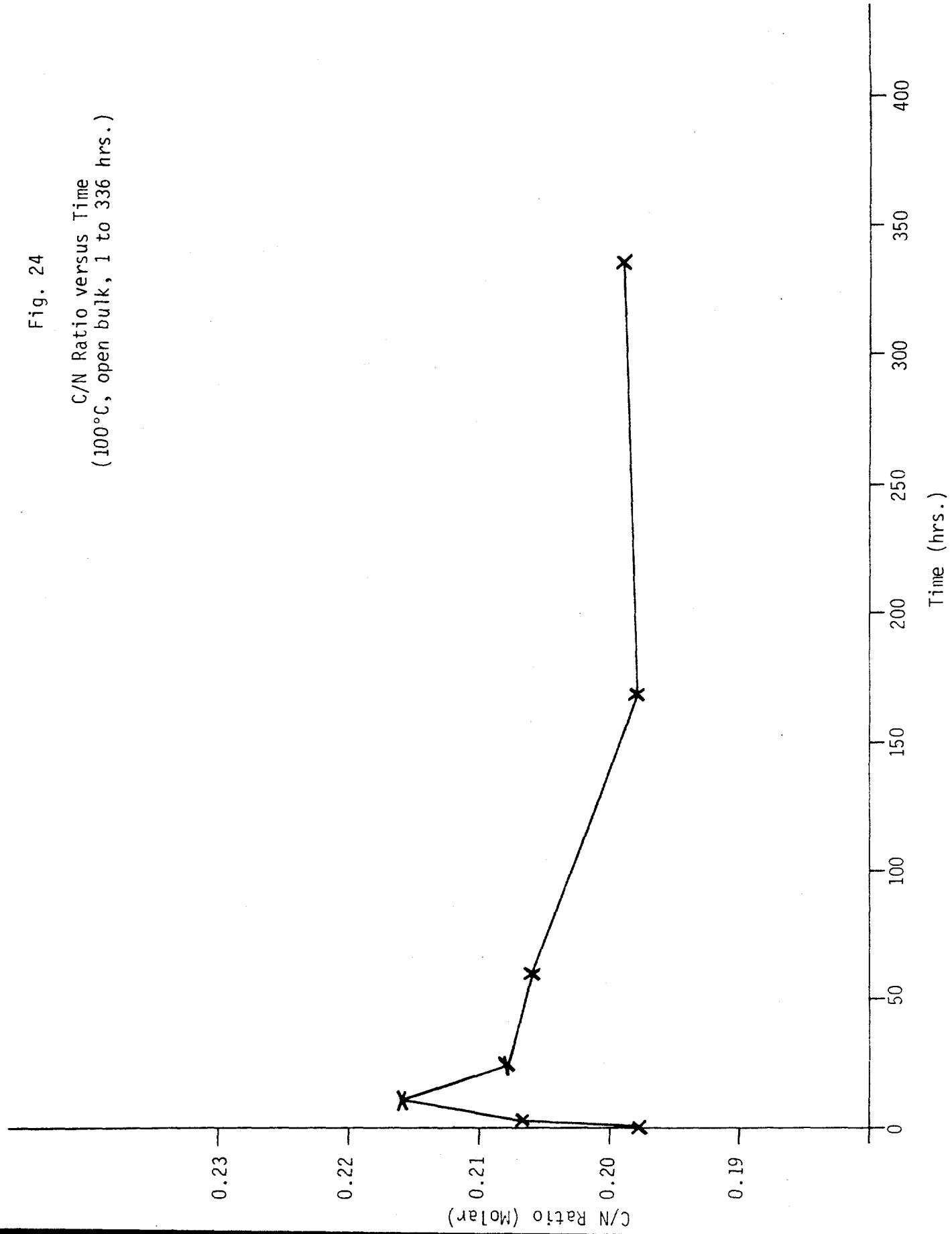
(d) 60 hrs.

(e) 168 hrs.

(f) 336 hrs.

Fig. 24

C/N Ratio versus Time
(100°C, open bulk, 1 to 336 hrs.)



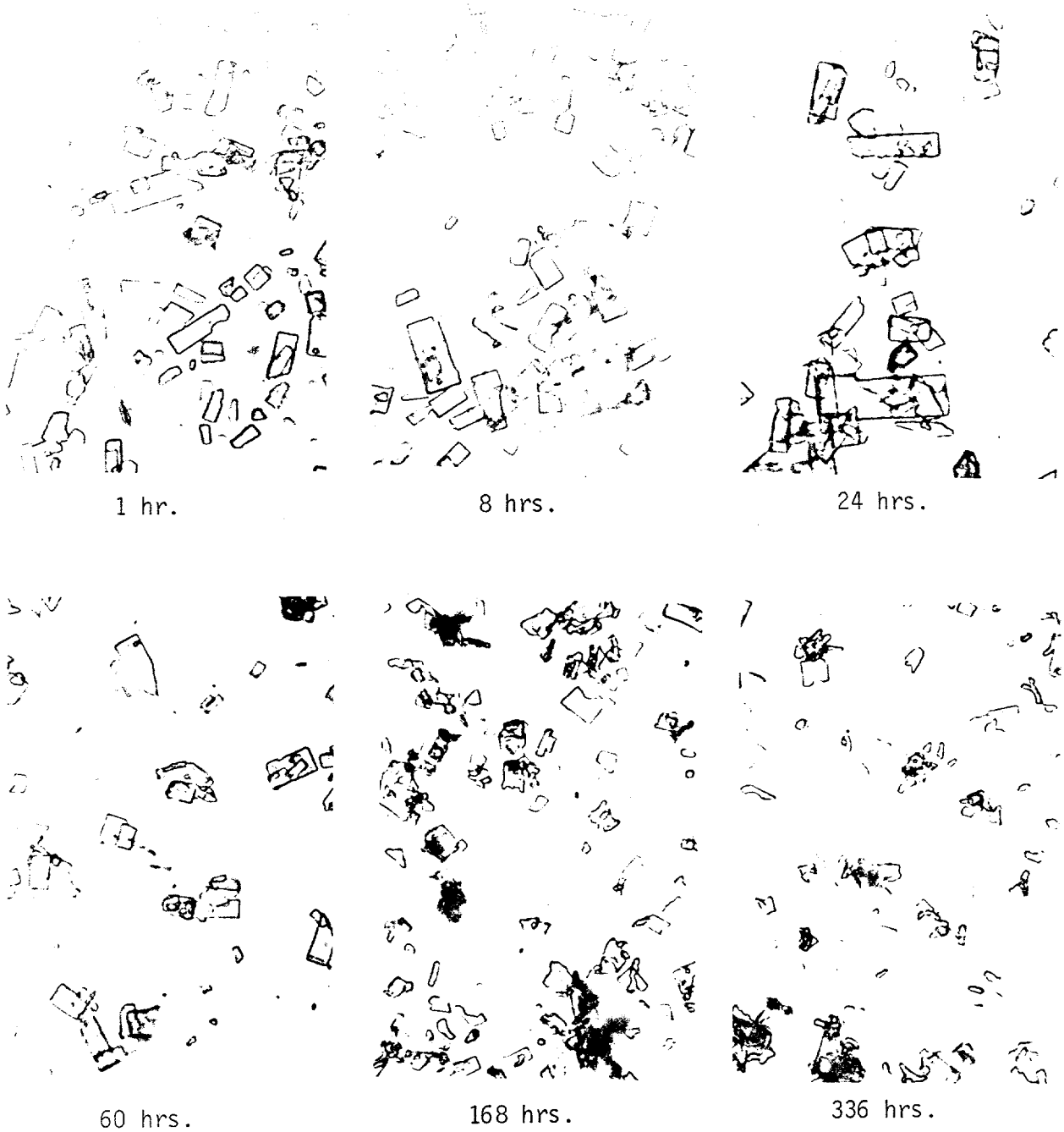


Fig. 25

Photomicrographs of CATCP 3-3-I Residues (X925)
(100°C, open bulk configurations)

Thermal Group VI (120°C, open bulk) - This group consisted of open bulk configurations heated at 120°C for periods extending from 1 to 336 hours.

Table VIII

Results - Thermal Group VI

Temperature (°C): 120 Open bulk configuration Pressure: Atmospheric

	Time (hours)						
	0.0	1.0	8.0	24.0	60.0	168.0	336.0
Carbon (%)	3.08	3.11	3.28	3.18	3.31	3.14	3.13
Nitrogen (%)	18.10	18.20	19.37	19.12	18.94	18.84	18.90
Hydrogen (%)	4.00	3.99	3.53	3.78	3.30	3.55	3.67
C/N Ratio	1/5.04	1/5.01	1/5.06	1/5.15	1/4.91	1/5.15	1/5.18
Surface Area (m^2/gm)	25.5	21.7	40.1	36.3	33.0	32.7	42.3
Infrared Spectra, Fig. No.	1	26(a)	26(b)	26(c)	26(d)	26(e)	33(a)
DTA, Fig. No.	2	27(a)	27(b)	27(c)	27(d)	27(e)	27(f)
Photomicrographs, Fig. No.	-	29	29	29	29	29	29

Infrared spectral results [Figs. 1, 26(a-e)] indicate a nearly complete conversion from the terminal/bridged to the bridged cyano configuration after one hour at this thermal level (:C≡N-, ν_s, 4.51 μ).

However, the results from differential thermal analyses do show a dynamic condition in its thermal characteristics from 1 through 336 hours by the apparent change in the exothermic characteristics in the region of 275 to 320°C (Fig. 27).

Chemical analyses apparently follow the erratic exothermic thermal characteristics in regard to the residual carbon percentages (Table VIII). There does not appear

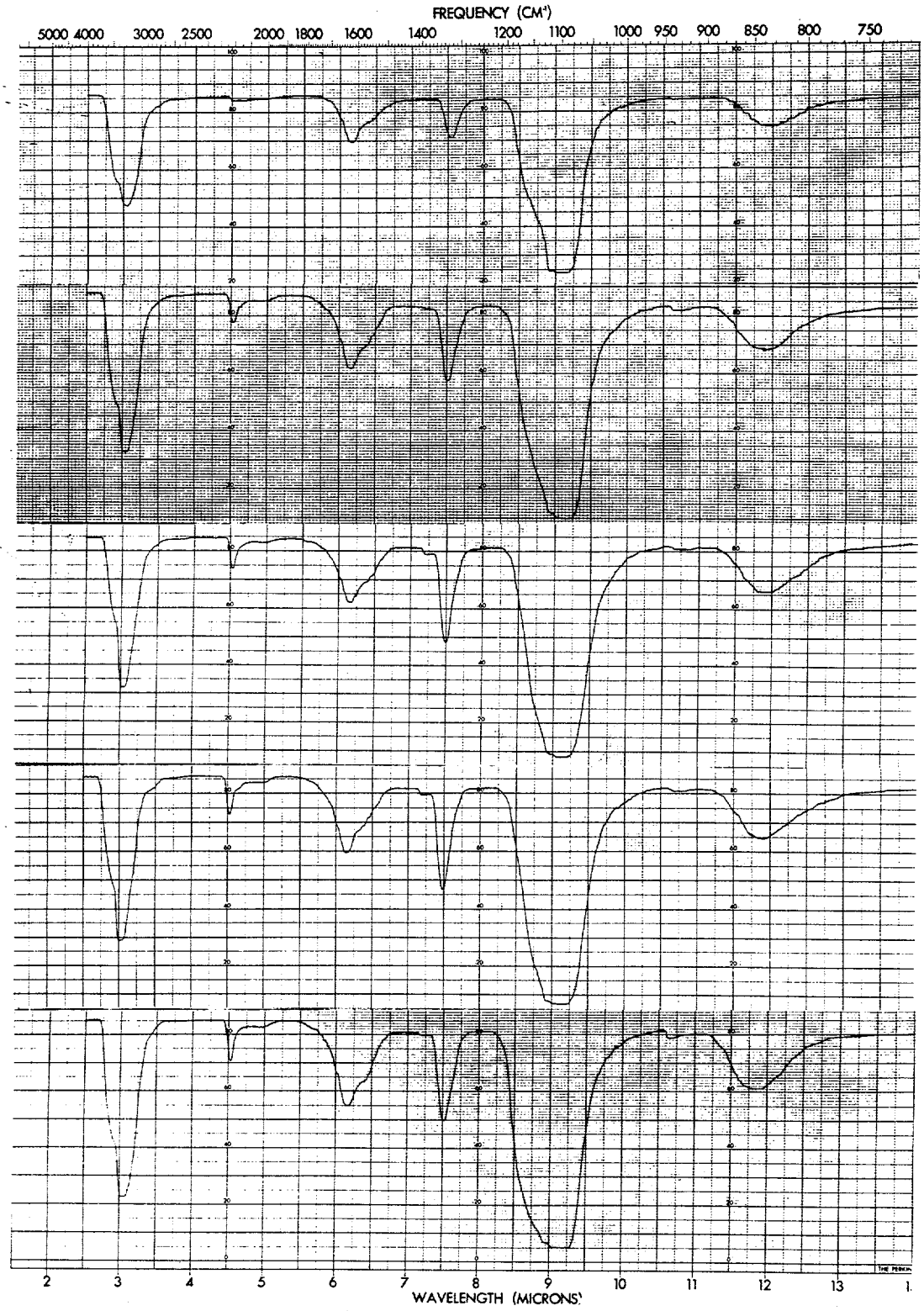
to be any obvious correlation between the fluctuating carbon percentages and the molar C/N ratios of the thermal residues (Fig. 28).

Surface area changes found in these residues as a function of the temperature-time composite show an extremely erratic pattern; decreasing at 1 hour, sharply increasing in the 8-hour residue, followed by a gradual decrease from the 8 to 168-hour residues, which in turn, is followed by a sharp increase in the surface area in the 336-hour residue (Fig. 29, Table VIII).

All indications as a result of the data obtained from the Group VI residues show a constant change occurring in the material, if not a change in functional group composition, then in the structural and/or functional group percentage composition.

Fig. 26

Infrared Spectra of CATCP Residues
(120°C, open bulk)



(a) 1 hr.

(b) 8 hrs.

(c) 24 hrs.

(d) 60 hrs.

(e) 168 hrs.

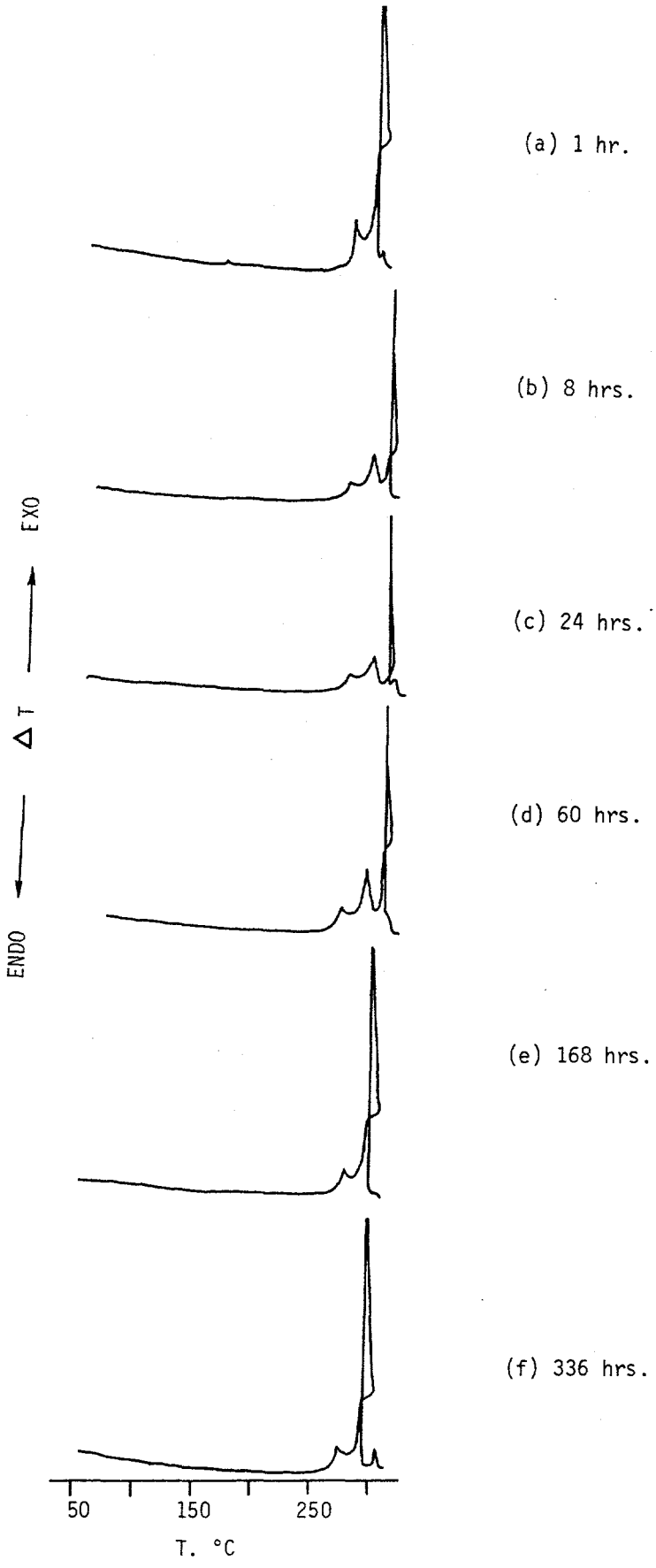
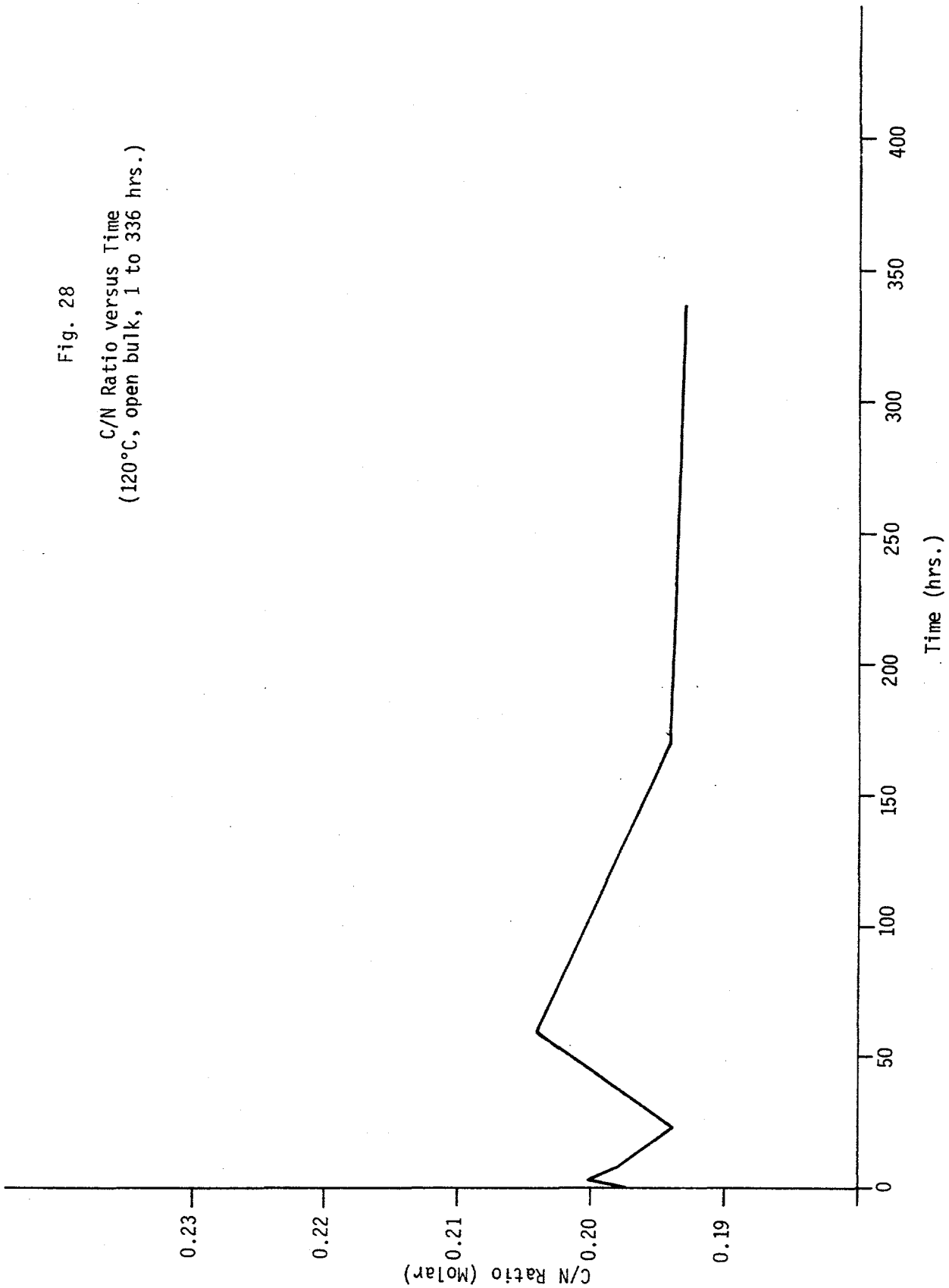
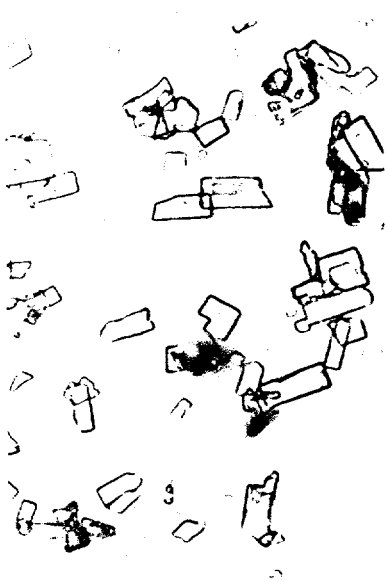


Fig. 27

DTA Thermograms of CATCP Residues
(120°C, open bulk)

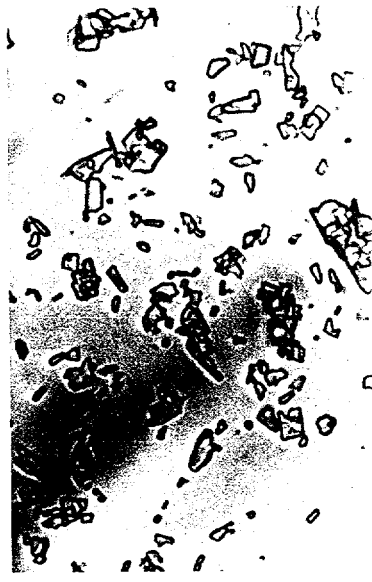
Fig. 28
C/N Ratio versus Time
(120°C, open bulk, 1 to 336 hrs.)





1 hr.

8 hrs.



24 hrs.

60 hrs.

168 hrs.

336 hrs.

Fig. 29

Photomicrographs of CATCP 3-3-I Residues (X925)
(120°C, open bulk configurations)

The relative change in the C/N ratio occurring up to 336 hours as a function of temperature is depicted in Fig. 30. The most important feature observed here is that, contrary to expectation, based upon the normally stronger bonding characteristics of the cyano group (C≡N) as opposed to the ammino group ($:NH_3$) the C/N ratio is seen to decrease as a function of temperature.

Infrared spectral analyses of 3-3-I residues, which have undergone thermal aging at 100°C for 336 hours under various system configurations, seem to maintain a consistency previously experienced, in that only the open system material converts to the bridged cyano (Fig. 31). Both the closed bulk and closed compact residues indicate the continued presence of the bridged/terminal cyano bonding (4.9, 4.6 μ). There also is definite indication of formation of an ammonium product(s) by the presence of absorption at ∿ 7.10 μ attributed to the degenerate deformation mode of NH_4+ (δ_d). As previously mentioned in this report, ammonium perchlorate was identified as a decomposition product in a limited sublimation study of the original 3-3-I.

Differential thermal analyses of the residues plainly show a marked difference in the exothermic characteristics of the closed bulk and closed compacted residues in the 275 to 315°C region (Fig. 32).

Chemical analyses give a resultant C/N molar ratio comparison of the closed bulk/closed compact of 0.193/0.207, indicating a compositional percentage increase in the closed bulk material. It may be noted here that the C/N molar ratio for the closed compacted residue from the 120°C, 336-hour study also has a value of 0.193.

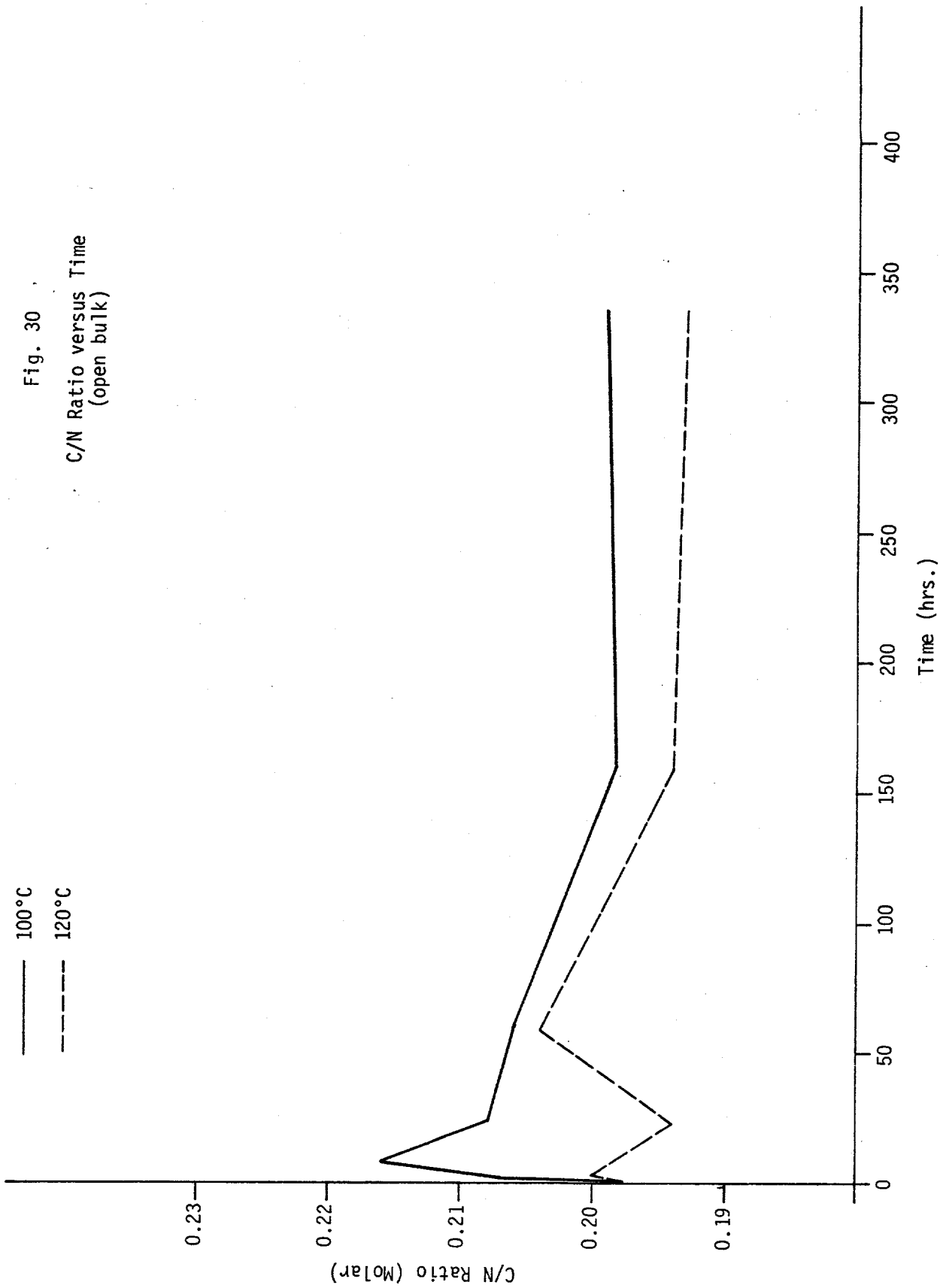
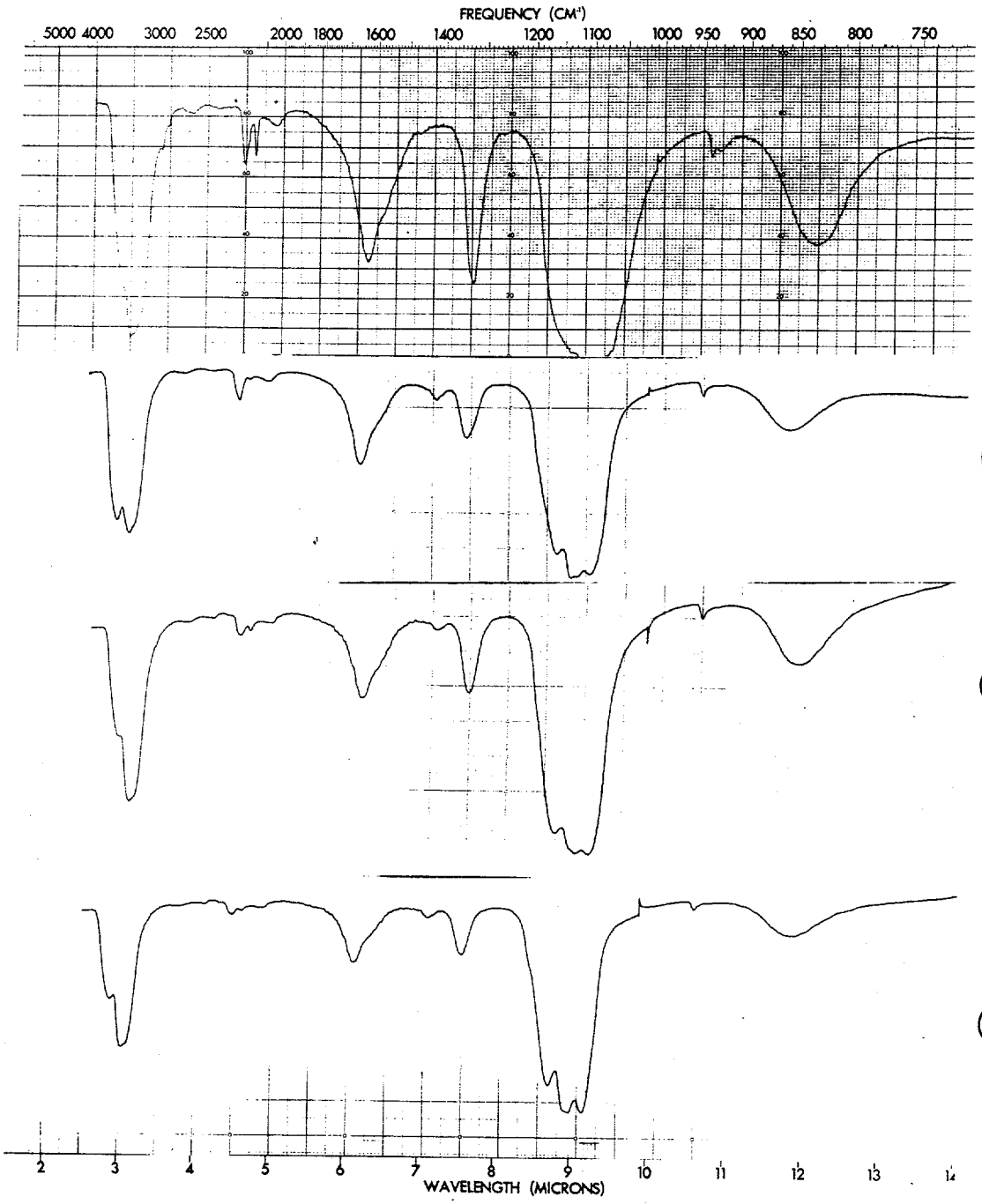
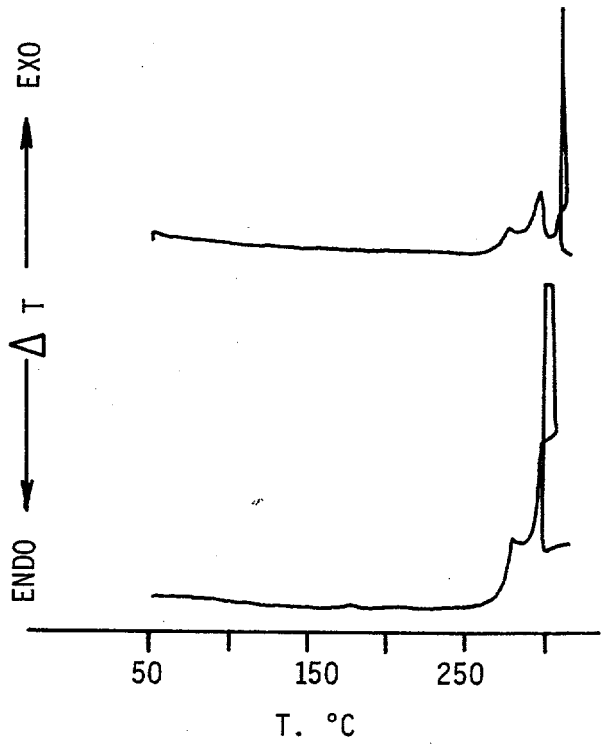


Fig. 30
C/N Ratio versus Time
(open bulk)

Fig. 31

Infrared Spectra of CATCP Residues
(100°C, 336 hrs.)





(a) closed bulk

(b) closed compact

Fig. 32

DTA Thermograms of CATCP Residues
(100°C, 336 hrs.)

Infrared spectral results (Fig. 33) obtained from thermal residues, which had undergone storage at 120°C for 336 hours in various system configurations, display the occurrence of cyano bridging in the open bulk material but maintain a bridged/terminal cyano configuration in the closed bulk and closed compact systems ($-C\equiv N$, ν_s, 4.9 and 4.6 μ). The presence of an ammonium product(s) is again indicated in the residues from both the open and the closed configurations (NH_4+, δ_d, ∿ 7.1 μ).

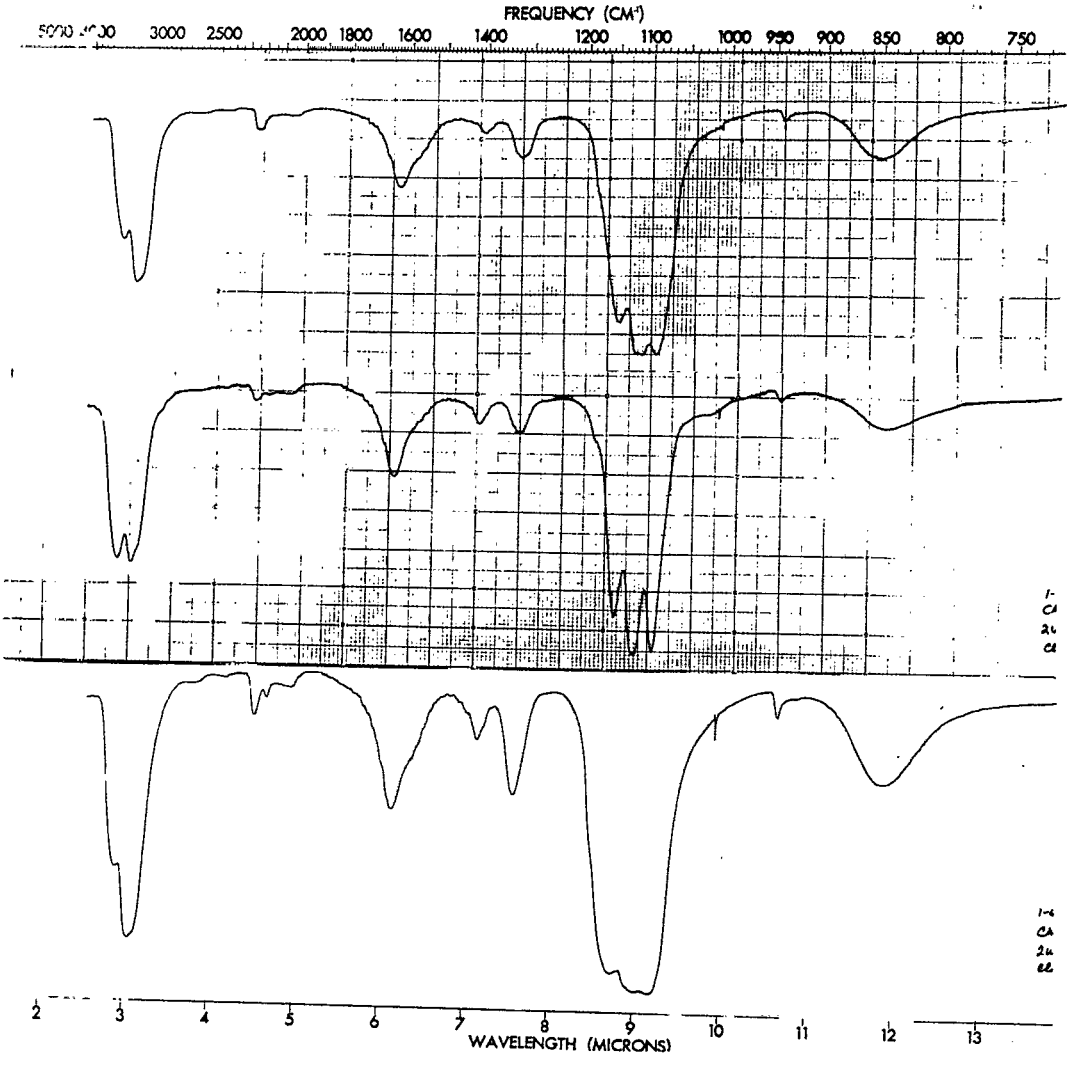
Differential thermal analyses results (Fig. 34) depict a substantial difference of the exothermic characteristics between the residues from the closed bulk and those from the closed compact systems, specifically in the region from 265 to 310°C.

The results of surface area measurements (gas adsorptometry) present divergent incremental paths for open bulk materials at 100°C and at 120°C for an aging period up to 336 hours (Fig. 35). Whereas the surface area change appears to approach zero as a result of the aging at 100°C for 168 hours, that for the material heated at 120°C continues to increase at an appreciable rate. Photomicrographs of these materials are presented in Fig. 36.

Surface area changes encountered as a result of compacting the material to a density of 0.85 gm/cc indicate only slight changes from the unheated configuration (Fig. 37, Table IX).

Fig. 33

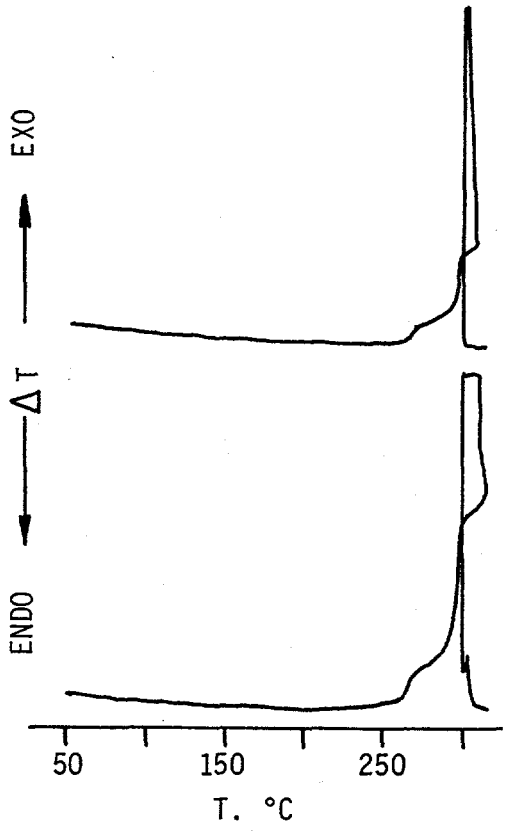
Infrared Spectra of CATCP Residues
(120°C, 336 hrs.)



(a) open bulk

(b) closed bulk

(c) closed compact



(a) closed bulk

(b) closed compact

Fig. 34

DTA Thermograms of CATCP Residues
(120°C, 336 hrs.)

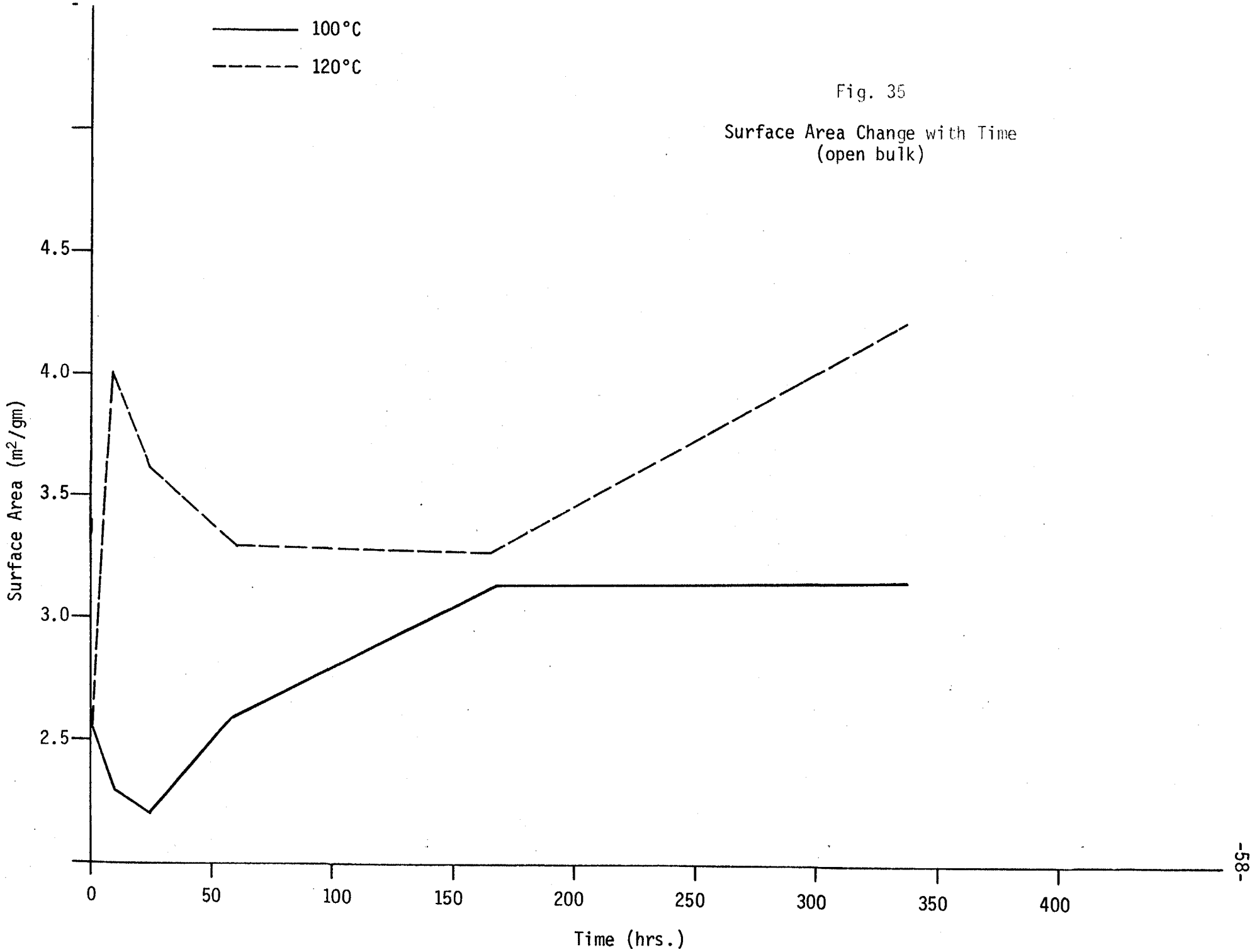


Fig. 35

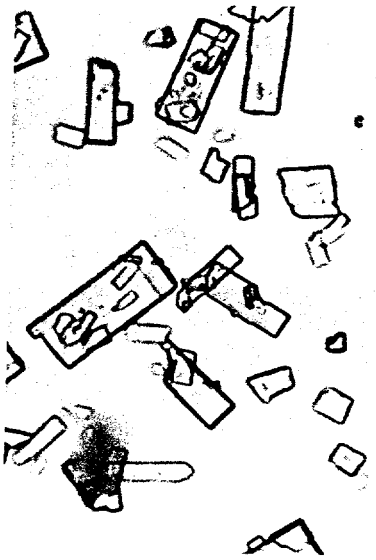
Surface Area Change with Time
(open bulk)

Original | 336 hrs. @ 100°C | 336 hrs. @ 120°C

Fig. 36

Photomicrographs of CATCP 3-3-I Bulk Samples (X925)

Original Bulk



Original Closed Compact

Closed Compact
(336 hrs. @ 100°C

Closed Compact
(336 hrs. @ 120°C)

Fig. 37

Photomicrographs of CATCP 3-3-I Compacted Samples (X925)

Table IX

Surface Area Change with Compaction

System Configuration	Temperature (°C)	Time (hrs)	Surface Area (m^2/gm)
Open bulk (unheated)	25	-	2.55
Closed compact (unheated)	25	-	2.18
Closed compact	100	336	2.21
Closed compact	120	336	2.38

An interesting result of the thermal aging of the 3-3-I material occurred in regards to a significant color change, which occurs in systems of the closed configurations the most radical change occurring in the systems of maximum boundary restraint and subjected to the greatest temperature-time composite (Fig. 38, Table X).

The sample color fidelity of Fig. 38 is poor; however, it is sufficient for the purpose of visual comparison of the residual materials.

Sufficient time was not available to comprehensively study the darkened material; however, it was found that the residue from the closed compacted system (120°C, 336 hours) was totally soluble in water and the residue from the closed bulk systems (120°C, 336 hours) was partially soluble in the same solvent. A silver nitrate ($AgNO_3$) test for the presence of uncoordinated cyano (CN) and/or ionic chloride (Cl) produced only marginal indications of a positive test.

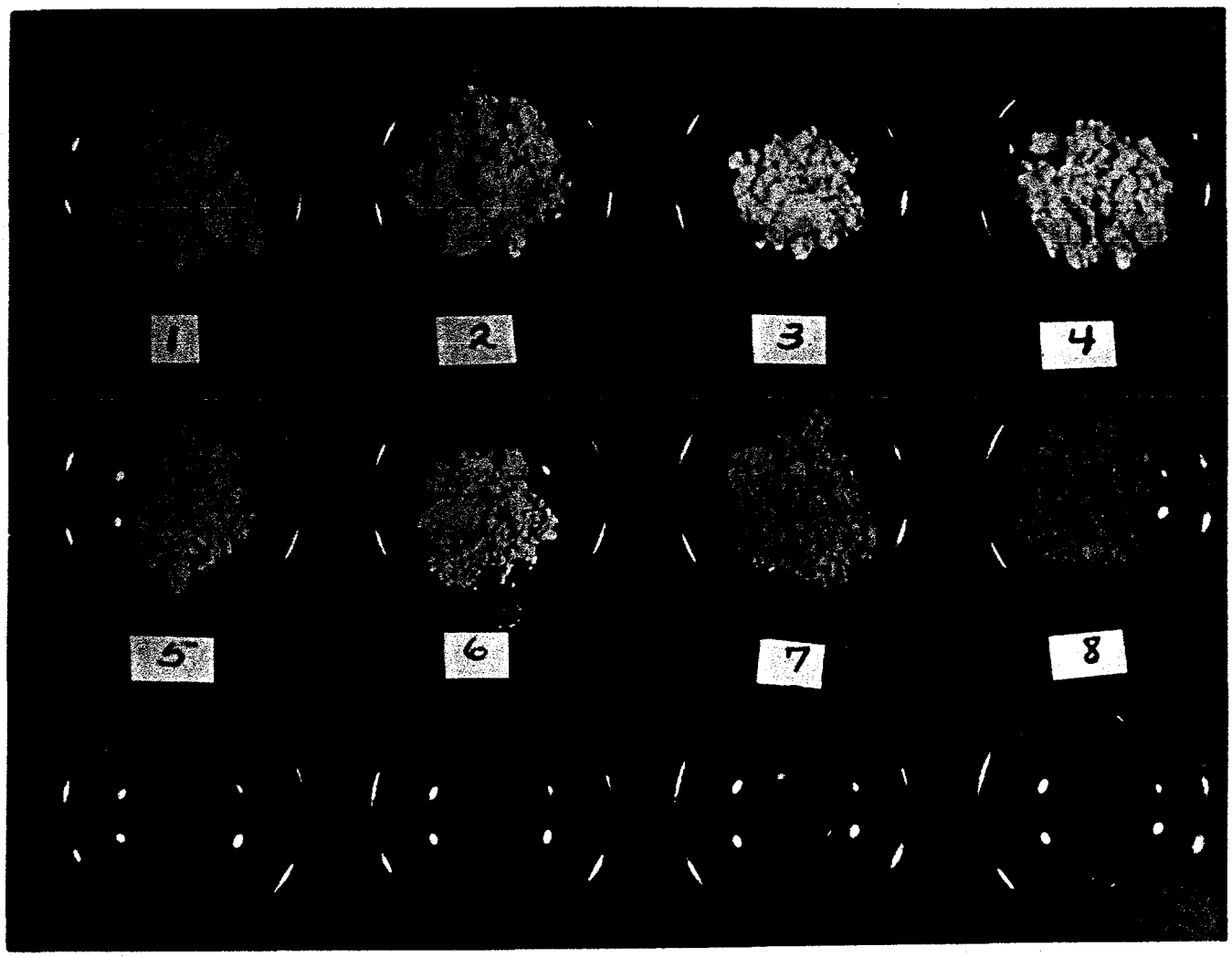


Fig. 38

Color changes of 3-3-I with thermal aging

Table X

Thermal History of 3-3-I Samples

Fig. No.	Configuration	Temperature, (°C)	Time, (hrs)
37-1	Original (bulk)	-	-
37-2	TF-AK	-	-
37-3	Closed bulk	70	20
37-4	Closed bulk	100	336
37-5	Closed compact	100	336
37-6	Open bulk	120	336
37-7	Closed bulk	120	336
37-8	Closed compact	120	336

ADDENDUM

Particle Characterization of CATCP By Zeiss Particle Size Analyzer

Sample	Predominant Shape (%)	Avg. Length (μ)	Avg. Width (μ)	Avg. Volume (μ^3)	Avg. Spherical Diameter (μ)	Avg. L/W Ratio	Avg. Particle Surface Area (μ^2)	Avg. Cross Sectional Area (μ^2)	Specific Surface Area (cm^2/gm)
Open bulk 1 hr. @ 100°C	91% Rectangular	1.997	1.333	1.739	1.374	1.448	9.360	2.817	26905
Open bulk 8 hrs. @ 100°C	60% Rectangular	1.925	1.337	1.132	1.229	1.638	7.100	2.256	31350
Open bulk 24 hrs. @ 100°C	63% Rectangular	1.882	1.345	1.249	1.253	1.535	7.493	2.388	29992
Open bulk 60 hrs. @ 100°C	92.8% Rectangular	1.866	1.331	1.595	1.350	1.358	8.788	2.624	27552
Open bulk 168 hrs. @ 100°C	44% Rectangular 36% Ellipsoidal	1.454	1.234	0.990	1.209	1.332	5.678	1.568	28678
Open bulk 336 hrs. @ 100°C	84% Rectangular	1.567	1.254	1.107	1.224	1.292	6.654	1.917	30061
Open bulk 1 hr. @ 120°C	70.2% Rectangular	1.810	1.314	1.265	1.226	1.472	7.379	2.368	29158

COMMENTS

The prominent features observed as a result of this study strongly indicate that, under the specific thermal and system boundary conditions imposed on the 3-3-I material, apparent total conversion of the bridged/terminal cyano material to the bridged configuration only occurs in the open system configurations. As a result of a definite material change, as experienced with closed systems which had undergone thermal aging at 120°C for 336 hours, it appears that the boundary restrictions imposed on these systems causes a significantly different reaction path to be taken than that by the material in the open configurations.

An ammonium product(s), indicated through infrared spectra to be a result of decomposition, is formed in all configurations which are accompanied by a sufficient thermal-time composite input, with ammonium perchlorate (NH_4ClO_4) identified as a decomposition product during the process of a limited sublimation study (120°C, 30 hours).

There is a leveling off in the rate of change in surface area for the open bulk material at 100°C at 168 hours, whereas the rate of change in surface area for the 120°C runs present a high rate of change continuing in this region up to 336 hours. However, the plateau effect seen for the 100°C material is inconclusive for the determination of surface area stability without further investigation of the material at longer periods, particularly in view of the fact that the results of differential thermal analyses show a proclivity for the thermally aged materials to continue to be in a dynamic condition in regards to their exothermic characteristics.

The results of Zeiss particle size measurements of the various thermal residues appear at the end of the discussion of this report. These data were not presented in the appropiate places in the main body of the report due to submission at too late a date.