Studies of Thermosetting Resin. I. The Infrared Analysis of Cured Epoxy Resins

By Tadao SUGITA and Mitsuko ITO

(Received January 18, 1965)

Recently many investigations of epoxy resins has been made. However, as analyses of thermosetting resins are generally difficult, a method of identifying the curing agents used has not yet been established for cured epoxy resins.

We have learned that the infrared analysis of pyrolyzates, which Harms1) has successfully applied with various resins and elastomers and McGarvey2) and Tanaka3,4) with elastomers only, is very useful for thermosetting resins. Therefore, we have applied this method, along with a more standard procedure, in the analyses of cured epoxy resins. Some studies5-10) of amine-cured resins performed by means of the infrared spectroscopic technique have been published, but only a single study11) has been reported on acid anhydride cured resins.

In the present paper, only cured epoxy resins which contain no other materials (e. g., fillers and plasticizers) will be studied. Infrared spectra are recorded for the powders of cured epoxy resins and their pyrolyzates as a means to establish a method of identifying the curing agents.

Although Harms identified the types of resins, he did not identify the types of curing agents in the case of epoxy resins. From the infrared spectra of the powders of cured epoxy resins, we can determine only whether the cured resin is an acid anhydride or an amine-cured type. However, from the spectra of the pyrolyzates of cured epoxy resins, we can readily identify the types of acid anhydrides which were used in the curing process.

---

1) D. L. Harms, *Anal. Chem.*, **25**, 1140 (1953).

2) J. W. McGarvey, *Technical Report* Nr. **58—2159.**, Rock Island Arsenal Laboratory, Illinois (1958).

3) T. Tanaka, *J. Soc. Rubber Ind. Japan* (*Nippon Gomu Kyokaishi*), **29**, 998 (1956).

4) T. Tanaka, H. Kano and H. Higashi, ibid., **30**, 762 (1957).

5) H. Lee and K. Neville, "Epoxy Resins," McGraw-Hill, New York (1957).

6) H. Dannenberg and W. R. Harp, *Anal. Chem.*, **28**, 86 (1956).

7) L. A. O'Neill and C. P. Cole, *J. Appl. Chem.*, **6**, 356 (1956).

8) D. E. Peerman, W. Tolberg and D. E. Floyd, *Ind. Eng. Chem.*, **49**, 1091 (1957).

9) C. E. Feazel and E. A. Verchot, *J. Polymer Sci.*, **25**, 351 (1957).

10) H. C. Anderson, PB **151150** (1957).

11) A. Shimazaki and M. Kojima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1610 (1963).

Here the infrared spectra of the pyrolyzates of seven acid anhydride-cured epoxy resins will be studied in detail.

Experimental

Measurements.—Spectra were scanned using a Perkin-Elmer Model 21 infrared spectrophotometer, with a sodium chloride prism in the 600 cm^{-1}-to-4000 cm^{-1} region.

The Preparation of Cured Epoxy Resins.—As the epoxy resin, Epon 828 (Shell Chemical Corp.) was used. Figure 1 shows the structures of Epon 828 and the curing agents. Table I shows the mixing composition and the curing conditions accepted as standard. The solid curing agent was stirred

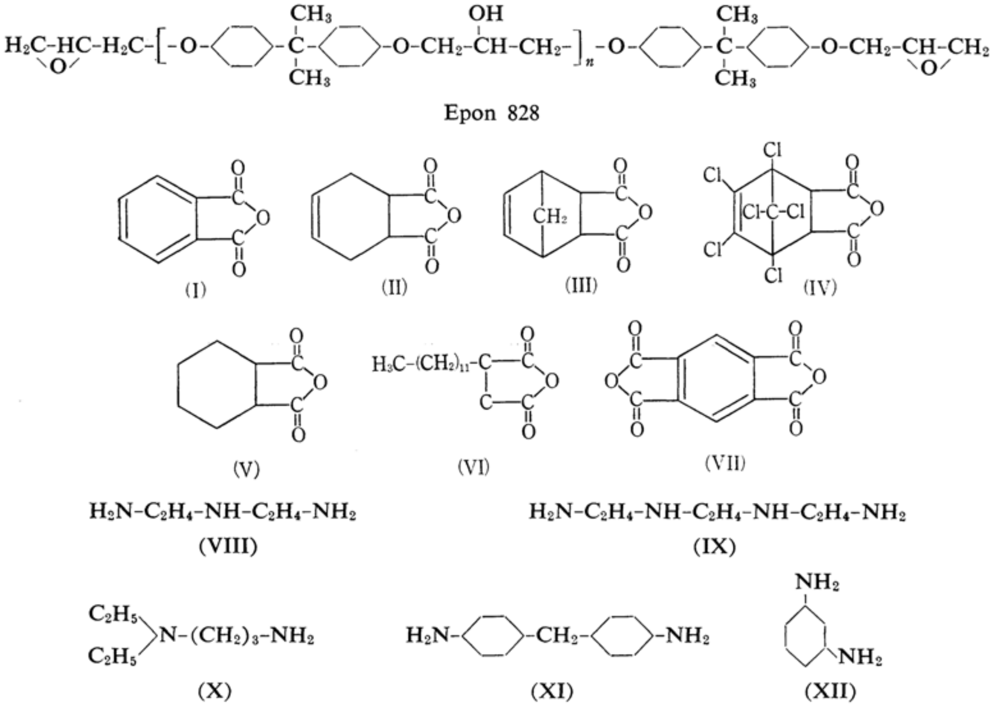

Fig. 1. Structure of Epon 828 and curing agents.
(I) Phthalic anhydride (PA). (II) Tetrahydrophthalic anhydride (THPA). (III) Endomethylenetetrahydrophthalic anhydride (EMTHPA). (IV) Chlorendic anhydride (HET). (V) Hexahydrophthalic anhydride (HHPA). (VI) Dodecenyl succinic anhydride (DDSA) (VII) Pyromellitic dianhydride (PMDA). (VIII) Diethylene triamine (DETA). (IX) Triethylene tetramine (TETA). (X) Diethylamino propyl amine (DEAPA). (XI) *p*, *p'*-Diamino diphenyl methane (DDM) (XII) *m*-Phenylene diamine (MPDA).

TABLE I. MIXING COMPOSITION AND CURING CONDITION

Type	Curing agent	Parts per 100 parts of Epon	Curing condition
Acid anhydride	PA	60	130°C 2 hr. + 150°C 10 hr.
	THPA	80	80°C 2 hr. + 150°C 4 hr.
	EMTHPA	80	80°C 2 hr. + 150°C 4 hr.
	HET	100	100°C 1 hr. + 200°C 1 hr.
	HHPA	80	80°C 2 hr. + 150°C 4 hr.
	DDSA	130	100°C 6 hr.
	PMDA	31	120°C 3 hr. + 220°C 20 hr.
Amine	DETA	8	20°C 2 hr. + 115°C 30 min.
	TTA	14	Room temp. 4 days
	DEAPA	8	115°C 1 hr.
	MPDA	14	100°C 1 hr. + 200°C 1 hr.
	DDM	27	150°C 2 hr. + 125°C 4 hr.

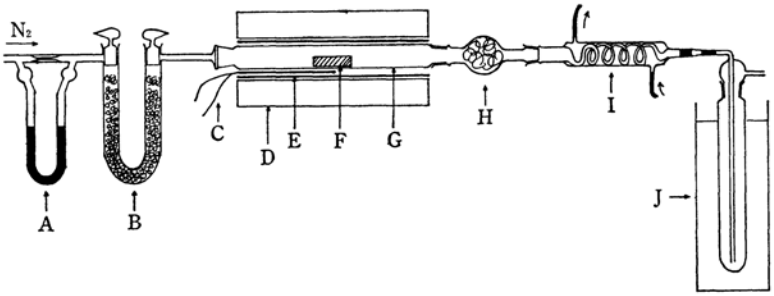

Fig. 2. Equipment of pyrolysis.

A	Flowmeter	F	Sample
B	U tube with silica gel	G	Borosilicate glass tube
C	Thermocouple	H	Air-cooled trap (with glass wool)
D	Electric Furnace	I	Water cooled trap
E	Porcelain tube	J	Freezing mixture trap

TABLE II. PROPERTIES OF PYROLYZATES

Type of acid anhydride		Spectrum number and pyrolysis temperature				
		I room temp. —300°C	II 300—350°C	III 350—400°C	IV 400—450°C	V 450—500°C
PA	Properties of pyrolyzates	Needles	Needles + Yellow liq.	Fine crystal + Yellow liq.	Yellow liq.	Yellow liq.
	Method of measurement	K ◎	K ◎	K	K	K
THPA	ibid.	White crystal	Pale purple liq.	Pale purple liq. + Brown liq.	Brown liq.	Brown liq.
	ibid.	K ◎	S	S	S	S
EMTHPA	ibid.	White crystal	Yellow liq.	Yellow liq.	Yellow liq.	Yellow liq.
	ibid.	K ◎	S	S	S	S
HET	ibid.	White crystal	Reddish purple liq.	Reddish purple liq. + Brown liq.	Yellow brown liq.	Yellow brown liq.
	ibid.	K ◎	S	S	S	S
HHPA	ibid.	Colorless liq.	Yellow liq.	Yellow liq.	Yellowish brown liq.	brown liq.
	ibid.	S	S ◎	S	S	S
DDSA	ibid.	Yellow liq.	Yellow liq.	Yellow liq.	Yellowish brown liq.	Yellowish brown liq.
	ibid.	S ◎	S ◎	S	S	S
PMDA	ibid.	Yellowish brown solid	Brown purple soild	Yellow brown liq. (a)+White solid (b)	Yellow brown liq. (a)+White solid (b)	Yellow brown liq.
	ibid.	K	K	S (a), K (b)	S (a), K (b)	S
None (Epon 828 only)	ibid.	Pale-yellow liq.	Pale-yellow liq.	Yellow liq.	Yellow liq.	Yellow liq.
	ibid.	S	S	S	S	S

* K KBr pellet technique, S Sandwich technique, ◎ Indicates the fractions utilized for identification of the curing agents used.

into warmed Epon 828, stirring was continued and the mixture was heated until the curing agent had been dissolved uniformly into the resin. The liquid curing agent was thoroughly mixed with the resin at room temperature. Then the sample was cured in an oven.

The KBr Pellet Technique of Cured Resins.—A file was used to reduce a block of cured resin to small particles. This method was found to be very simple and convenient for preparing a powdered sample for infrared analysis. The powdered sample thus obtained was passed through a 200 mesh screen. About 1 mg. of the sieved sample was thoroughly mixed with about 200 mg. of KBr powder, and a KBr pellet about 1 mm. thick was then prepared.

The Method of Pyrolysis.—Figure 2 shows the equipment of pyrolysis. About 2 g. of a sieved sample was placed into a horizontal borosilicate glass tube in an electric furnace. In the case of Epon 828, the sample was inserted into the furnace in a platinum boat. Then the temperature was raised at the rate of 2°C/min.; pyrolysis was continued until the temperature reached 500°C under a stream of high-purity nitrogen at a flow rate of 32 cc./min. Pyrolysis products were trapped in five temperature sections: (I) room temperature to 300°C; (II) 300—350°C; (III) 350—400°C; (IV) 400—450°C, and (V) 450—500°C (Table II). As can be seen from Fig. 2, three traps, the air-, water- and dry ice-cooled traps, were connected in series. Liquid and crystalline pyrolyzates caught in the traps were washed out with acetone. After the acetone had evaporated, the infrared spectra were recorded using the KBr-pellet technique or the sandwich technique.

Results and Discussion

The infrared spectra of Epon 828 (the top of Fig. 5) and acid anhydrides (the top of Figs. 6 through 12) used as curing agents were recorded for reference. All anhydrides show two characteristic carbonyl absorption bands near 1780 and 1850 cm^{-1}.

The Infrared Spectra of Cured Epoxy Resins.—In the case of the amine-cured resins, a hydroxyl group is formed by the reaction of the amine with the epoxy group. Accordingly, the absorption band of the epoxy group at 907 cm^{-1} disappears and the absorption intensity of the hydroxyl group in the 3400 cm^{-1} region increases. Examples of two spectra (DETA- and MPDA- cured resins) are shown in Fig. 3. The spectra of three other types (DEAPA-, TTA- and DDM-cured resins) give patterns very similar to the first two (DETA and MPDA). Therefore, while the spectra of these cured resins can not be used to identify the specific type of amine utilized as the curing agent, the characteristic pattern can be used to determine that an amine and not an anhydride was used in the curing process.

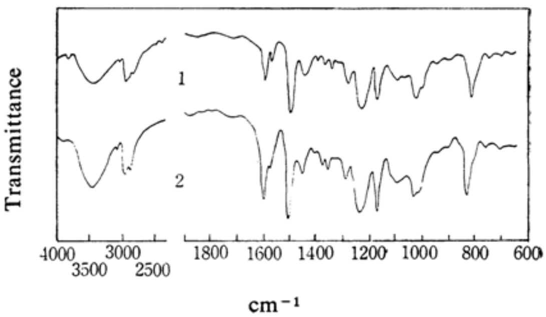

Fig. 3. Spectra of amine cured epoxy resins.
1 DETA-cured resin
2 MPDA-cured resin

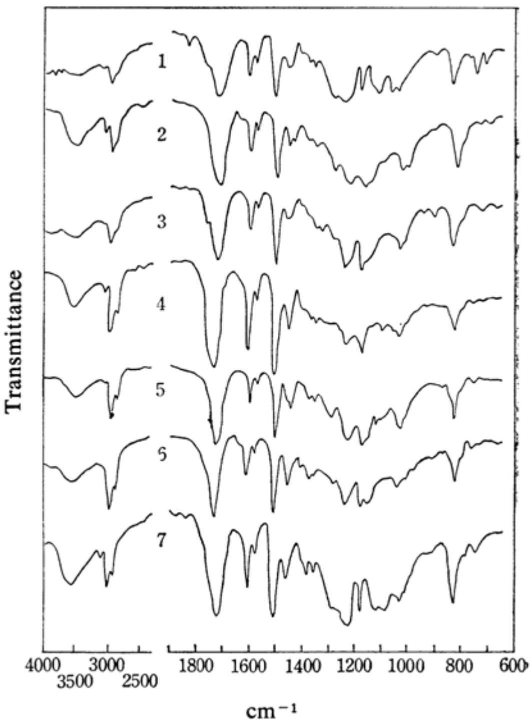

Fig. 4. Spectra of acid anhydride cured epoxy resins.
1 PA-cured resin
2 THPA-cured resin
3 EMTHPA-cured resin
4 HET-cured resin
5 HHPA-cured resin
6 DDSA-cured resin
7 PMDA-cured resin

In the case of acid anhydride-cured resins (Fig. 4), an ester-linkage is formed by the reaction of the anhydride with the hydroxyl group and an acid with the epoxy group, while a further ether linkage is formed by the reaction of the epoxy group with the hydroxyl group. Therefore, the absorption band of the epoxy group at 907 cm^{-1} disappears and a strong ester carbonyl band appears at 1730 cm^{-1}.

Furthermore, small differences in the spectra are observed for each acid anhydride in the 1300—1000 cm^{-1} region. The spectra of these anhydride-cured resins can not be utilized to identify the types of anhydrides used as curing agents, but they are useful in determining whether or not the resin is an anhydride-cured epoxy resin by the form of the curve, especially through the presence of a strong carbonyl band.

The Infrared Spectra of Pyrolyzates of Cured Epoxy Resins.—As the amounts of pyrolyzates caught in the water- and dry ice - cooled traps were very small, their infrared spectra were not studied. Most of the pyrolyzates caught in the air-cooled trap were studied by means of their infrared spectra. As can be seen from the properties of the pyrolyzates (Table II) and their infrared spectra (Figs. 6 through 12), pyrolyzates of PA-, THPA-, EMTHPA-, and HET-cured epoxy resin obtained at room temperature through 300°C were crystalline, and their infrared spectra gave nearly the same patterns as those of the individual acid anhydride-curing agents. Meanwhile, the pyrolyzates of HHPA- and DDSA-cured epoxy resins obtained at room temperature through 350°C were liquid, and each of the acid anhydride-curing agents used could be identified by the finger-print region of their infrared spectra.

In the spectra of the pyrolyzates of HHPA-cured resin, the formation of aliphatic compounds was observed. In the case of PMDA-cured resin, the infrared spectra of pyrolyzates did not give the pattern of PMDA utilized for curing at a low pyrolysis temperature, but did give the specific pattern at a high pyrolysis temperature; this pattern was different from those shown in the cases of other acid anhydride-cured resins. The ordinary acid anhydride used as a curing agent can be identified by the characteristic curve shown by the infrared spectra of pyrolyzates, while the presence of PMDA as a curing agent may be presumed from the fact that the spectra of the pyrolyzates do not have the absorption bands of PMDA, in contrast with the other acid anhydride-cured resins.

The experimental results with Epon 828 and each acid anhydride cured-epoxy resin will be discussed in detail below.

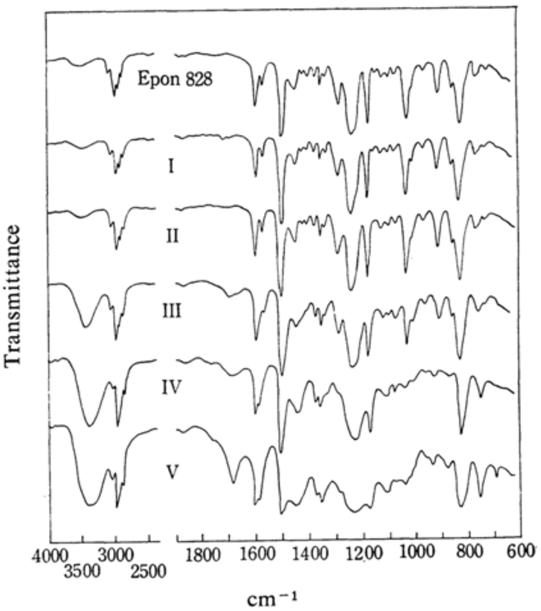

Fig. 5. Spectra of Epon 828 and its pyrolyzates.

Epon 828 (Fig. 5).—Epoxy resin itself was also investigated as a related study. The infrared spectrum of the pyrolyzate obtained at room temperature through 350°C is almost the same as that of the original sample. At temperatures above 350°C, the intensities of the absorptions at about 3400 cm^{-1} (νOH) and 1700 cm^{-1} (νC=O) increase. At temperatures above 400°C the intensities of the absorptions at about 1025 cm^{-1} (ether linkage ν C–O–C) and 907 cm^{-1} (stretching vibration of epoxy ring) decrease; the characteristic spectrum is obtained from the sample at temperatures between 400—450°C.

This typical spectrum appears in every spectrum of the pyrolyzates above 350°C of cured epoxy resins subsequently mentioned, and so it is referred to as the *characteristic spectrum* hereafter. From these spectra, the opening of epoxy rings, the scission of ether linkages and the formation of hydroxyl groups may be assumed.

The main absorption bands of this *characteristic spectrum* are assigned as follows: 755 cm^{-1}: CH out-of-plane vibration of the mono-substituted benzene ring; 830 cm^{-1}: CH out-of-plane vibration of the para-substituted benzene ring; 1240, 1514 and 1610 cm^{-1}: vibrations related to the benzene ring; 1695 cm^{-1}: C=O stretching vibration.

Further, when an ethyl alcohol solution of 2, 4-dinitrophenylhydrazine acidified with hydrochloric acid was added to an ethyl alcohol solution of fractions IV and V, brown oily products separated out. From this fact and from the absorption near 1695 cm^{-1} in spectra IV and V, the formation of carbonyl compound may be assumed.

PA-Cured Resin (Fig. 6).—Spectrum I is the same as that of PA. Pyrolyzate II is a mixture of a crystalline and a yellow liquid material, but except for the absorption of PA, only the absorption of the hydroxyl group (near 3400

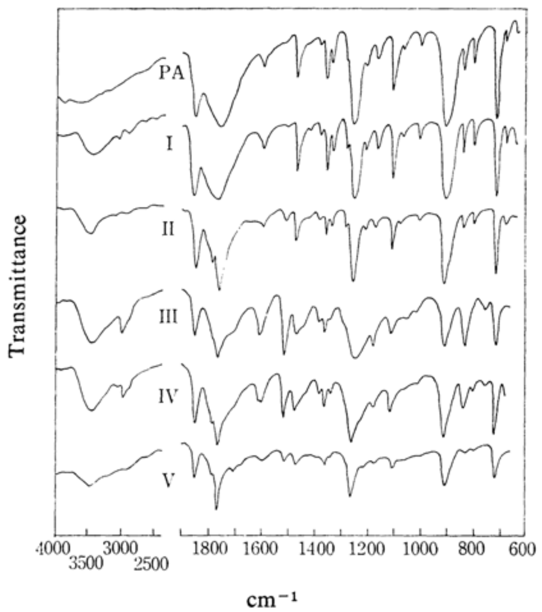

Fig. 6. Spectra of PA and pyrolyzates of PA-cured resin.

cm^{-1}) appears. Pyrolyzate III and IV show the absorptions of PA (at 1845, 1763, 1107, 905, and 715 cm^{-1}) overlapped with the *characteristic spectrum.* From the absorption as a shoulder at 1700 cm^{-1} the formation of a carboxyl group may be assumed. Even in spectrum V the absorptions of PA (at 1845, 1763, 1260, 905, and 715 cm^{-1}) are clearly observed.

THPA-Cured Resin (Fig. 7).—Spectrum I is nearly the same as that of THPA. In spectrum II the absorptions of THPA are also observed at 1831, 1770, 1179, 1090, 995, 964, 933, 772, and 730 cm^{-1}. In spectrum III the *characteristic spectrum* strongly appears, while the absorptions of THPA are not clearly observed. The absorption curve becomes broad in spectrum IV.

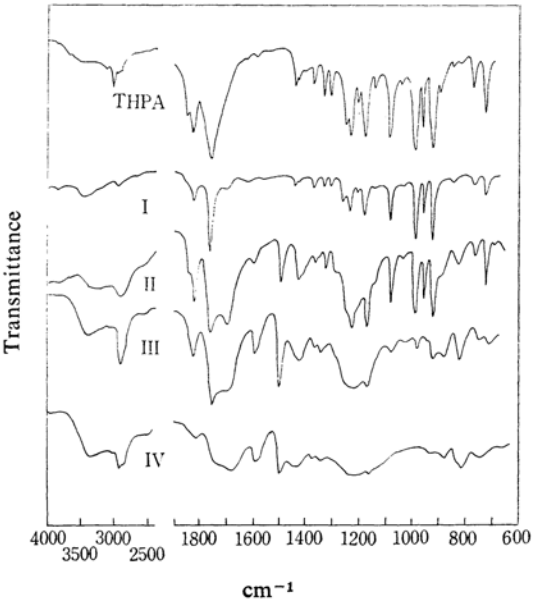

Fig. 7. Spectra of THPA and pyrolyzates of THPA-cured resin.

EMTHPA-Cured Resin (Fig. 8).—In spectrum I the absorption bands at 1860, 1770, 1335, 1293, 1117, 1078, 910, 791, and 732 cm^{-1} are identical with those of EMTHPA. In spectra II, III, and IV the *characteristic spectrum* appears strongly, but the absorptions of EMTHPA could not be clearly observed. However, unlike the case of PA and THPA, the higher the pyrolysis temperature, the lower the carbonyl band shifts in the wave numbers of the spectrum (for example, 1725, 1717, 1695 and 1680 cm^{-1} in II, III, IV and V respectively).

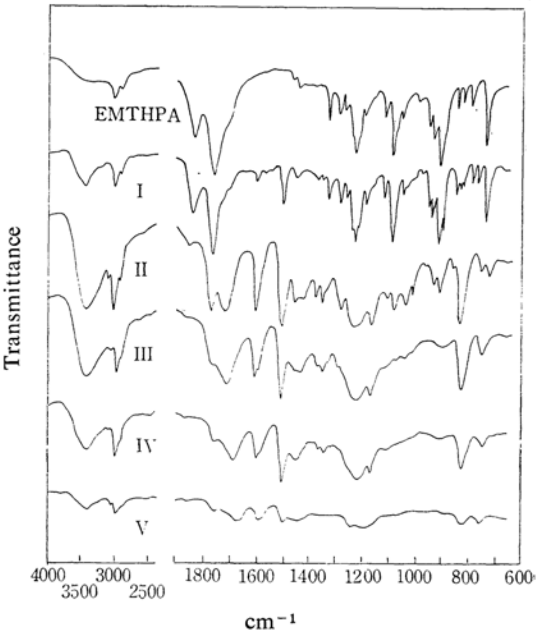

Fig. 8. Spectra of EMTHPA and pyrolyzates of EMTHPA-cured resin.

When an ethylalcohol solution of 2, 4-dinitrophenylhydrazine acidified with hydrochloric acid was added to the fractions from I to V, yellow oily products separated out, except for fraction I.

The amount of the products is highest in fractions III and IV. From this fact and from the above-mentioned carbonyl band shifts, the formation of a carbonyl compound may be assumed.

HET-Cured Resin (Fig. 9).—Pyrolyzate I is crystalline, and HET is identified by the absorptions at 1883, 1782, 1598, 1243, 1216, 1067,

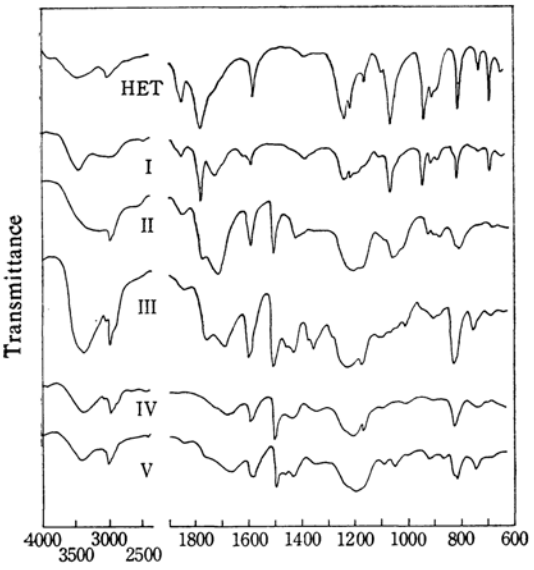

Fig. 9. Spectra of HET and pyrolyzates of HET-cured resin.

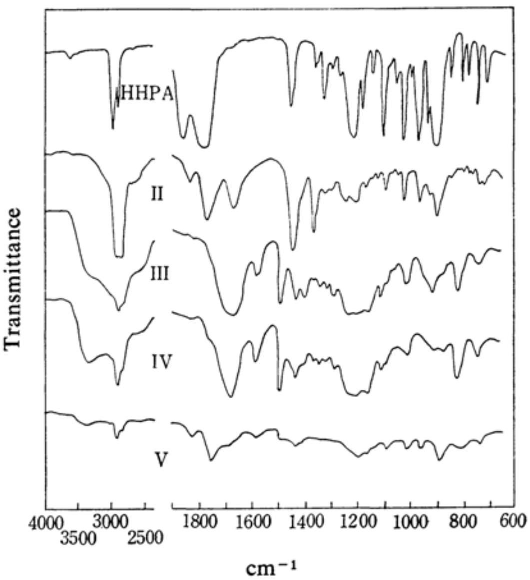

Fig. 10. Spectra of HHPA and pyrolyzates of HHPA-cured resin.

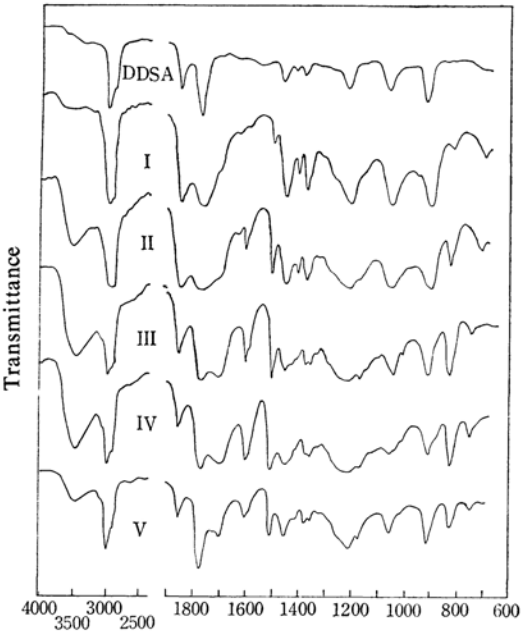

Fig. 11. Spectra of DDSA and pyrolyzates of DDSA-cured resin.

942, 817, and 695 cm^{-1}. The *characteristic spectrum* becomes strong in the spectra of the sample obtained above 300°C; the absorption bands of HET could not be identified. Similarly, in the case of EMTHPA, at the higher pyrolysis temperatures, the carbonyl band shifts to a lower wave number (for example, 1725, 1722, 1692, 1680, and 1675 cm^{-1} in I, II, III, IV and V respectively).

In this case 2,4-dinitrophenylhydrazine test was omitted, but the formation of a carbonyl compound may be assumed.

HHPA-Cured Resin (Fig. 10).—The amount of pyrolyzate I was too small to get a satisfactory spectrum. From spectrum II HHPA is identified by the absorptions at 1841, 1780, 1100, 1027, 971, and 900 cm^{-1}. Furthermore, strong absorption bands appear near 2800, 1450, and 1380 cm^{-1}. From this fact, the formation of aliphatic chain compounds by the opening of the cyclohexane ring of HHPA may be assumed. The *characteristic spectrum* becomes strong in the spectra of the samples obtained above 350°C. Furthermore, in contrast with other acid anhydrides, the carbonyl bands of this acid anhydride could not be observed, while the carbonyl band appears strongly near 1675 cm^{-1}. After several experiments, it was recognized that the two carbonyl bands of HHPA appeared when the spectra were measured immediately after the pyrolysis. Therefore, a high reactivity of HHPA was assumed.

DDSA-Cured Resin (Fig. 11).—As DDSA is a liquid with an aliphatic chain, its pyrolyzate is also a liquid, as would be expected. DDSA is identified from spectra I and II. With a rise in the temperature of the pyrolysis, spectra III, IV, and V give a pattern similar to the *characteristic spectrum.*

PMDA-Cured Resin (Fig. 12).—The spectra of pyrolyzates I and II are almost identical with the *characteristic spectrum.* Pyrolyzate III is a mixture of liquid and a small amount of

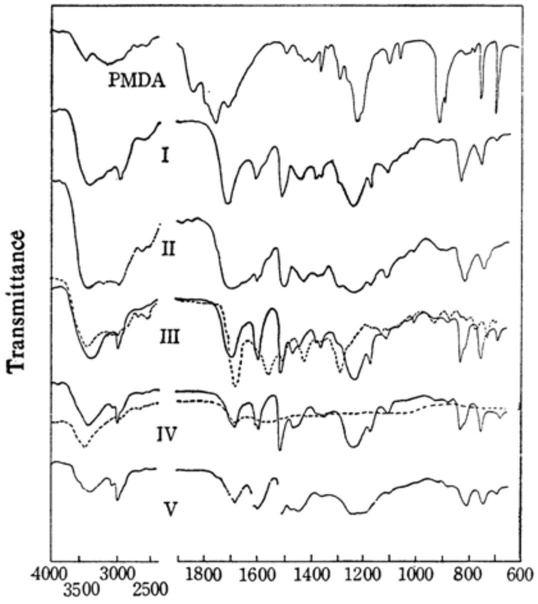

Fig. 12. Spectra of PMDA and pyrolyzates of PMDA-cured resin.
III, IV: — liquid, --- solid

solid. The liquid portion gives almost the same spectra as the pyrolyzates I and II. Meanwhile, the spectrum of the solid portion is very specific, but it has not been identifide as yet. Only in the case of PMDA-cured resin is the original acid anhydride used as a curing agent (PMDA) not formed by pyrolysis. However, PMDA can be assumed by a comparison of the pyrolyzate spectra of PMDA-cured resin with those of another acid anhydride resins.

Summary

To pulverize the cured hard resins for the infrared KBr technique, the method using a file is very simple and convenient.

From the infrared spectra of the powder of cured epoxy resins using the KBr-pellet technique, the curing agent used can be readily identified by type whether it is an amine or an acid-anhydride type by the absence or presence of the carbonyl absorption band.

Furthermore, in the case of the acid anhydride-cured epoxy resins, the acid anhydride used as the curing agent can be identified by type from the spectra of the resin pyrolyzate. Namely, PA, THPA, EMTHPA, HET, and DDSA may be identified immediately from the spectra of pyrolyzates between room temperature and 300°C, and HHPA, from the spectrum of the pyrolyzate between 300 and 350°C. The results of these experiments are summarized in Table II.

PMDA used as a curing agent can not be so straightforwardly identified as in the other cases, but even this may be identified by a comparison of the spectra of the pyrolyzates of PMDA-cured resin with those of the pyrolyzates of each resin.

The authors are indebted to Dr. Shigeyuki Tanaka, Associate Professor of the University of Tokyo, for his helpful advice and comments.

Central Research Laboratory
Fuji Electric Co., Ltd.
Nagasaka, Yokosuka