ROYAL AIRCRAFT ESTABLISHMENT

TECHNICAL NOTE No. CPM. 47

SOME PHYSICAL PROPERTIES OF TERPHENYL RESIN BONDED LAMINATES

by

B. Nixon

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SUMMARY

The production of heat resistant thermosetting resins based on terphenyl and p. xylylene dichloride in various ratios is described. The strength of the laminates made from these resins is shown not to differ greatly and it is concluded that the cross-linking density remains the same for the three ratios investigated.

The resistance of asbestos laminates to gamma radiation and strong alkali is investigated, together with some preliminary strength tests on glass reinforced laminates.

Infrared spectrophotometry shows that the methylene groups within both terphenyl and polybenzyl resins are oxidised during ageing at elevated temperatures.

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1 INTRODUCTION

The exploitation of the Friedel-Crafts reaction between aromatic hydrocarbons and dichloromethyl derivatives has led to promising heat resistant polymers[1]. A useful inexpensive polymer is that based on a mixture of ortho meta and para terphenyls (Santowax R.) and some of the properties of asbestos reinforced laminates were given in a preliminary report[2].

It was noted during this investigation that the laminates displayed some initial thermoplasticity, which disappeared on ageing at elevated temperatures. It was appreciated that this could be partly due to low cross-linking density and it was realised that a more detailed investigation would be required to resolve this point.

It was decided to prepare terphenyl resins with different molar ratios of terphenyl to p. xylylene dichloride, and to investigate their physical properties. Additionally the physical properties of asbestos reinforced laminates bonded with these different resins would be determined.

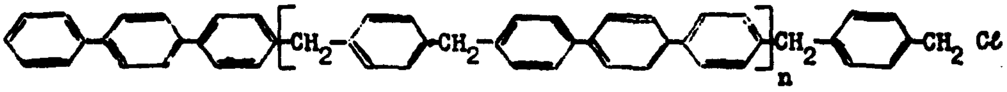
Preliminary investigations of glass cloth laminates have been made using the resin with the most suitable ratio of terphenyl to p. xylylene dichloride as found above.

A further point of interest from the initial report was the weight increase which followed heating in air at temperatures above 200°C. The process was followed by infrared spectrophotometry and evidence for oxidation of the methylene groups is presented.

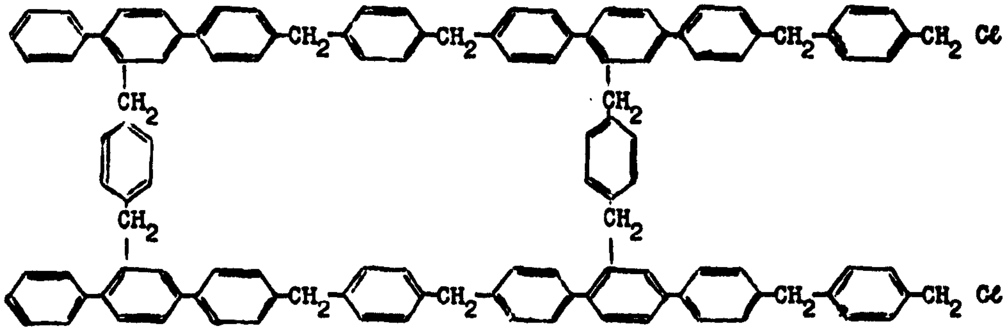
2 SYNTHESIS OF TERPHENYL RESINS

2.1 Theory

By using a 1:1 molar ratio of terphenyl to p. xylylene dichloride a linear polymer of the following structure should be produced:



Additional p. xylylene dichloride should bring about cross-linking leading to the following structure.



By increasing the ratio of p. xylylene dichloride to terphenyl, it was thought that a greater cross-linking density, hence greater strength, and less thermoplasticity at elevated temperatures could be obtained in the finally cured resin[2]. From previous experience it was felt that the ratios 10:11, 10:13, 10:15 of terphenyl to p. xylylene dichloride were the most suitable for comparison.

The resin could be made in two stages. In the first stage a ratio of 4 moles of terphenyl to 3 moles of p. xylylene dichloride was used, so producing a thermoplastic resin and then this resin could be reacted with a further amount of p. xylylene dichloride to give a highly branched resin that would cross-link on further heating.

2.2 Practice

The resin was made in two stages. The first stage resin was made in the melt at 150°-180°C, while the second stage was made in a suitable solvent in order to give a solution of the thermosetting resin in any of the three ratios to be investigated.

2.2.1 First stage resin

15·36 moles (3533 grams) of Santowax R, a commercially available form of the mixed terphenyls and 11·4 moles (1997 grams) of p. xylylene dichloride were heated together (Table 1). The 10 litre reaction vessel, which had a wide neck to facilitate the pouring of the liquid resin, was fitted with a powerful stirrer, a thermocouple lead, an argon supply to prevent oxidation of the reactants and a straight through condenser, connected to a receiving vessel containing a known amount of alkali.

When both the reactants had melted they were kept at 150-180°C. The catalyst, 5·0 mls of 10% w/w stannic chloride in 1.2 dichloroethane was added at intervals when it was noticed that the hydrogen chloride evolved had slowed down. The hydrogen chloride was dissolved in water and neutralised against twice normal (2N) sodium carbonate, using bromo-phenol blue as an indicator (Fig.1). Towards the end of the reaction, the temperature of the reactants was increased to 180°C in order to assist the pouring of the resin, this was when 80% of the theoretical amount of hydrogen chloride had been evolved.

The first stage resin had a softening range of 80-95°C and when fresh was a clear red and transparent, but on several days standing it became green and opaque. The resin was typically thermoplastic, and should have a molecular weight in the region of 1000 to 1200.

On two occasions a crude pilot-plant batch of p. xylylene dichloride was used to make the resins, but the reaction was so violent that it became uncontrollable and gelled[3]. Upon investigation it was found that the p. xylylene dichloride was contaminated with a strong catalyst, so increasing its reactivity that even the p. xylylene dichloride could cross-link itself. Upon purification by further recrystallisation the p. xylylene dichloride behaved in the normal manner.

2.2.2 Second stage resin - small scale

The second stage resin was made on a small scale in order to find out how much hydrogen chloride could be evolved before gelation. This was done with all the three ratios investigated (Fig.2).

50·2 grams of the first stage resin was dissolved in 120 grams of 1.2 dichloroethane (Table 1). The flask was fitted with an air supply to sweep over the hydrogen chloride evolved through a straight condenser to the receiving vessel containing known amounts of alkali. When the resin had dissolved the appropriate amount of p. xylylene dichloride was added (Table 1). The whole was gently boiled. When the p. xylylene dichloride had dissolved, a little catalyst was added and a steady flow of hydrogen chloride was evolved. The acid was titrated against 2N sodium carbonate using bromo-phenol blue as indicator.

All the samples of this second stage resin gelled after between 1·95 and 2·22 grams of hydrogen chloride had been evolved, regardless of reactants ratios employed.

2.2.3 Second stage resin - large scale

This large batch of the second stage resin was only taken approximately 60% of the way towards gelation, so that a solution of a potentially thermosetting resin was obtained.

900 grams of the first stage resin was dissolved in 2560 grams of 1.2 dichloroethane in a 10 litre flask fitted as in the small scale preparation. When the first stage resin had dissolved the appropriate amount of p. xylylene dichloride was added, then the whole was gently boiled. A little catalyst was added and the hydrogen chloride evolved was titrated against the alkali.

After approximately 60% of the total possible hydrogen chloride had been evolved this second stage resin was cooled. This resin would be used either diluted with 1.2 dichloroethane to impregnate the asbestos felts or used undiluted to impregnate the glass fabric.

3 FABRICATION OF BOARDS

3.1 Asbestos laminates

The boards, 12 inches square and approximately 1/10th of an inch thick were made by using five asbestos felts for each. The appropriate amount of the second stage resin was diluted with more 1.2 dichloroethane so as to make a solution having a solids content of between 10 and 12%.

Each piece of asbestos felt was weighed and impregnated with the appropriate amount of diluted resin to give a resin content on the cured boards of 50%. The "A" direction[+] was marked on the felts which were then left to dry in air at room temperature for at least 24 hours.

Sets of five felts were used to make each board. The felts were assembled with the grain direction parallel and cured at 185°C and 500 lb/sq in. for 90 minutes, using steel platens coated with stearate grease. A powerful extraction system was fitted to the press in order to remove the hydrogen chloride evolved during the cure, particularly when the board was vented at 30, 60 and 90 second intervals. The boards were left to cool under pressure until their temperature fell below 100°C. Each board was post cured for 72 hours at 200°C. During the post cure it was noticed that large amounts of p. xylylene dichloride sublimed onto the walls of the post curing oven when the 10:13 ratio resin and especially the 10:15 ratio resin had been used for the impregnation.

3.2 Glass laminates

Glass laminates were made using satin weave glass cloth with three different finishes (Marglass heat cleaned, Marglass 717, and Fothergill and Harvey NOL-24).

Four strips of each glass cloth 36" × 9" × 0·006" were impregnated with the undiluted second stage resin made using a 10:11 molar ratio of terphenyl to p. xylylene dichloride, and left to dry in air. Each laminate was made by using eleven plies of the impregnated cloth 7¼" square and cured in a frame mould (Fig.10) at 185°C for 90 minutes at a pressure of approximately 20 lb/sq in. The laminates were cooled under pressure and then post cured for 24 hours at 180°C and for 120 hours at 200°C.

4 STRENGTH TESTS AND PHYSICAL PROPERTIES

The following tests were carried out on the asbestos laminates made with ratios of terphenyl to p. xylylene dichloride of 10:13 and 10:15 -

Flexural strength at room temperature and at elevated temperatures, density, resin content and loss in weight of the laminates.

The above properties for the laminates made using the resin with the 10:11 ratio are taken from Technical Note CPM 8 [2]. In addition to the above properties, the resistance of these laminates to strong alkali and radiation was also investigated.

The glass laminates were cut into flexural strips and tested both at room temperature and at 240°C after ageing at 240°C for up to 1000 hours. Density, resin content and loss in weight were also determined.

4.1 Flexural strength at room temperature

The flexural strength of the specimens at room temperature was determined on a three point bending rig (based on the recommendations laid down in B.S.2782, Part 3, Method 304B, and in A.S.T.M. Specification D.790-59T) built into a large oven (see Appendix 1). A two inch span width was used throughout the testing and typically five specimens were tested in each group. Testing was carried out on each set of heat aged specimens (Tables 2 and 5-7).

4.2 Flexural strength at elevated temperatures

The flexural strength of the specimens at elevated temperature was determined on the same rig as was used to determine their strength at room temperature.

Short term ageing, up to 100 hours, was done entirely within the testing oven; long term ageing was carried out in separate ovens, the specimens being transferred to the oven rig at least one hour before testing. The temperature of the oven was controlled to within 2°C of the testing temperature (Tables 3 and 6-7).

4.3 Density

The density of the specimens was determined by weighing and measuring the flexural specimens (Tables 4 and 8).

4.4 Resin content

Resin contents were determined on the flexural specimens, after they had been broken, by ashing to constant weight at 800°C on a Stanton thermobalance[1] (Tables 4 and 8). In the case of the asbestos laminates allowance was made for the loss of weight of the asbestos itself[5].

4.5 Weight loss on laminates

Weight loss on the laminates was determined on the flexural specimens for different times at 200°C, 240°C and 300°C (Table 8, Fig.3).

4.6 Resistance to alkali

To observe the effect of strong alkali on the laminates, flexural specimens were immersed in 40% sodium hydroxide or 40% potassium hydroxide at room temperature and at 50°C.

The specimens removed after each period of ageing were washed thoroughly in running water and dried in an air oven at 50°C so that they were completely dry and alkali free. The flexural strength of the specimens was determined on the three point bending rig. The figures are given in Table 5 and graphically in Fig.4.

The good retention strength of terphenyl laminates after 4000 hours exposure to alkali is similar to that to be reported by Moore[6] for polybenzyl laminates. Both these Friedel-Craft resins are superior to conventional phenolic resins using the same reinforcement[6].

4.7 Resistance to radiation

In view of the high aromatic content of the terphenyl resin it should display good radiation resistance. For this reason it is of potential interest as a structural material in atomic energy applications.

In order to obtain evidence on this point flexural specimens taken from an asbestos laminate made with the 10:11 molar ratio resin were subjected to 10, 100 and 500 megarad doses of gamma radiation at the Royal Military College of Science, Shrivenham. After each dosage the specimens were tested on the three point bending rig at room temperature and at 240°C (Table 6).

5 INFRARED SPECTROPHOTOMETRY

It has been noticed with several resins that during the ageing at elevated temperatures of both the resins and the laminates an increase in weight occurs[1,2]. The most obvious explanation for this increase in weight is that the methylene group $-CH_2-$ is being oxidised to a carbonyl group $-C=O$.

Infrared spectrophotometry is well suited to following such chemical changes during a series of operations[7].

Both a terphenyl and a polybenzyl resin were tested to see whether their methylene groups could be detected initially and whether on exposure to heat these groups were replaced by the corresponding carbonyl groups.

A solution of the thermosetting resin was poured onto a sodium chloride disc and the solvent allowed to evaporate at 50°C to produce a clear film. The disc was mounted in a frame holder which was kept in the same position throughout the series of recordings. An initial spectrum was taken, then further spectra were recorded after 1 hour at 185°C, a second hour at 300°C, and finally after prolonged exposure (ca. 24 hours).

A series of standards were used to verify the positions of the main absorption peaks:-

(a) Santowax R. was used because of its aromatic groups.

(b) p. xylylene dichloride showed the methylene chloride groups (CH_2Cl).

(c) 1.2. dichloroethane, again for its methylene groups and because it was the solvent used.

(d) Benzophenone for the presence of the aryl ketonic groups.

The above spectra can be seen in figures 6 to 9 inclusive.

6 DISCUSSION OF RESULTS

On comparing the resins made in the different ratios it should be noticed that regardless of the amount of p. xylylene dichloride present, the gelation point is approximately the same in all cases (Fig.2). It was also noticed that large white crystals of p. xylylene dichloride could be seen under a low power microscope, in the gelled resin, especially in the higher ratio resins. p. xylylene dichloride sublimed from the laminates during their post cure.

At 200°C the flexural strengths of the terphenyl laminates from the three resins are quite similar, reaching their maximum cold strength after at least 1000 hours of ageing, while their strength at 200°C seems to be at a maximum between 1000 and 2000 hours.

Remembering that both the phenolic laminates - R.A.7 [4] and the terphenyl laminates made from the 10:11 ratio resin were aged at between 230°C and 240°C, whereas the other terphenyl laminates were aged at 240°C, then their flexural strengths cannot be compared directly. The only comparison that can be drawn is between two sets of laminates made from the resins of higher molar ratio, and these are obviously quite similar.

At 300°C, although all the specimens were aged in the same oven, but at different times, the severity of the temperature seems to degrade the laminates at roughly the same time - 75 to 100 hours.

All the laminates had low hot strengths at the beginning of each exposure schedule, but all improved during the subsequent ageing.

Weight losses of the three sets of laminates at 200°C were similar, at 230-240°C the laminates from the higher ratio resins lost more weight than the laminates made from the lower ratio, again on account of the former being aged at a lower temperature than the latter. At 300°C the laminates with the higher ratio resins tended to lose weight more rapidly than the other laminates.

The resistance of terphenyl laminates to strong alkali are given in Table 5 and Fig.4. From those results it can be seen that the terphenyl laminates retain at least 74% of their original flexural strength even after 4000 hours immersion in the strongest of alkali. The best phenolic laminates in this respect, R.A.1. could only retain 50% of their original flexural strength after the same exposure, and were below 74% before 500 hours of immersion had been attained[6].

The apparent resistance of terphenyl/asbestos laminates to gamma radiation is encouraging, as there appeared to be no detrimental effect after a dosage of 500 megarad. In view of this a series of longer exposures using glass reinforced laminates has been started.

Little work has been done so far on glass laminates, but even so some useful information has been obtained. The resin content, densities and weight losses of the laminates are all similar, but the flexural strengths vary considerably before and during ageing at 240°C.

The laminate containing glass fabric having the NOL -24 finish had the best initial cold strength, but it also had the poorest initial hot strength. After 100 hours at 240°C, at which time it could be assumed that each laminate had reached its optimum properties, the heat cleaned fabric laminate had the best overall strength properties. After 1008 hours ageing all three laminates had similar flexural strengths at 240°C. Laminates with a hot flexural strength of 24,000 lb/sq in. after 1000 hours at 240°C are good compared with present polyester and epoxy laminates[8].

Laminates made with the heat cleaned fabric always broke cleanly during testing, whereas in the other laminates the specimens were often delaminated. It was also noticed that the NOL-24 finished glass laminates did not tend to warp as much as the other two during ageing at 240°C.

It can be seen from Table 8 that the glass reinforced laminates lose much less weight at 240°C than the asbestos laminates at the same temperature. As all the weight loss must be the actual terphenyl resin, than after 1000 hours at 240°C approximately 7 to 12% of the resin within the laminate is lost, while 14% to 20% of the resin within the asbestos laminates is lost (average of the two higher ratio resins).

Taking the terphenyl and polybenzyl resins in Figs.7 and 8, their methylene groups ($-CH_2-$) can easily be detected by their strong absorption peaks at 2926 cm^{-1} and 2853 cm^{-1} together with peaks at 1465 ± 20 cm^{-1} (Figs.7a and 8a), which are similar to the absorption peaks produced by the methylene groups in p. xylylene dichloride and 1.2. dichloroethane (Figs.6b and 6c). On exposure to elevated temperatures the concentration of methylene groups decreases and there is a corresponding increase in the strength of the absorption peak in the region of 1670-1660 cm^{-1} (Figs.7 and 8), which corresponds to the carbonyl groups absorption range[9] as can be seen in the spectrum of benzophenone (Fig.9). There is a much broader but less convincing range for a carbonyl structure at 1200 ± 100 cm^{-1} which can be seen in the later spectra of both resins and in benzophenone.

7 CONCLUSIONS

The main conclusion to be drawn from the present work is that no matter what quantity of p. xylylene dichloride is used in the manufacture of the resins, the gelation point and the cross-linking density remain unchanged. The fact that free p. xylylene dichloride is observed when the higher ratio resins are gelled and also during the post cure of the laminates at 200°C, seem to point to the fact that any excess p. xylylene dichloride takes no part within the resin or the laminates.

Increasing the proportion of p. xylylene dichloride to terphenyl makes no difference to the initial hot strength of the laminates and only long ageing at elevated temperatures is effective in giving a reasonable hot strength. It can be assumed that the extra p. xylylene dichloride does not increase the cross-linking density at all.

The resistance of terphenyl laminates to sodium and potassium hydroxide is excellent, and the resistance to gamma radiation is very encouraging. Further work is in progress to confirm the radiation resistance of terphenyl bonded glass laminates on prolonged exposure.

The glass laminates can be made with reasonable ease, but a much larger programme should be undertaken to study the effects of different finishes of the glass cloth on the resultant laminates.

It seems clear that the methylene groups in both the terphenyl and polybenzyl resins are slowly oxidised to carbonyl groups by ageing at elevated temperatures in air. This contrasts with the findings of Conley and Bieron[7], who found rapid oxidation of the methylene groups to carbonyl groups in phenolic resins exposed to oxidative conditions.

In order to study in detail all the properties of terphenyl bonded laminates, large scale production of the resin and impregnated materials will have to be done, and suitable arrangements are being worked out with commercial organisations.

8 WARNINGS

Attention is drawn to the toxic hazards involved in handling *p.* xylylene dichloride, 1.2 dichloroethane and hydrogen chloride[10].

It is advisable to use barrier creams on exposed areas of skin and to have adequate ventilation during the impregnation and curing of the felts.

ACKNOWLEDGMENTS

Acknowledgments are made to Professor A. Charlsbury of R.M.C.S. for the use of his irradiation facilities and to Dr. W.A.Lee for his confirmation on the interpretation on the infrared spectra. The author also wishes to thank Mr. R.G.Hulme for the preparation of many hundreds of test specimens.

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ATTACHED:-

Appendix 1
Tables 1-8
Figs.1-12, Drgs Nos. CPM/R.271-279
Negs Nos. 164,934-164,936
Detachable abstract cards

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APPENDIX 1

USE OF HIGH TEMPERATURE FLEXURAL RIG

The flexural strength (cross breaking strength) of the laminates was measured both at room temperature and at elevated temperatures on the same apparatus (Figs.11 and 12). The conditions of testing were governed by B.S.2782, Part 3, Method 304b, and by A.S.T.M. Specification D.790.59T.

The specimen is placed across the two supports and the load is applied across the centre of the specimen by means of a piston actuated by a normal factory air supply system. The loading rate can be varied by means of the regulator valve so that the specimen will break within 15 to 45 seconds of applying the load. A maximum load pointer shows the exact breaking load recorded through the load gauge.

The actual procedure is as follows:-

(a) Specimen is placed across the two supports.

(b) Open main air supply tap.

(c) Leave tap A open and close tap C.

(d) Tap D should be open to the atmosphere, while tap B is closed.

(e) The regulator tap is slowly opened and the piston forces the plunger onto the load cell, which is connected to a gauge showing the load being applied, while the regulator gauge only shows the air line pressure.

(f) When the specimen breaks, taps B and C should be opened, and tap D is closed. The piston will then return to the top of the cylinder. The breaking load is recorded on the load gauge.

(g) The regulator valve is turned off and the broken specimen removed. During elevated temperature testing the load cell should be removed from the top of the loading plunger, as heat affects the instrument.

$$\text{Flexural strength} = \frac{3SL}{2BT^2}$$

S = Span between the supports.

L = Breaking load.

B = Width of specimen in inches.

T = Thickness of specimen in inches.

TABLE 1

First and second stage resin - Weights of reactants

	First stage resin			Second stage resin								
Reactants	Moles ratio	Ratio M.W.	Wgt.used (grams)	Moles ratio	Ratio M.W.	Wgt.used (grams)	Moles ratio	*Ratio M.W.	Wgt.used (grams)	Moles ratio	Ratio M.W.	Wgt.used (grams)
Terphenyl (Santowax R)	4·0	920	3533	10	2300	3533	10	2300	3533	10	2300	3533
p. xylylene dichloride	3·0	525	1997	11	1925	2960	13	2275	3490	15	2625	4030

Note:- If the entire batch of the first stage resin is used in the second stage, then 963, 1493 and 2033 grams of p. xylylene dichloride would be needed to change the ratio of 4:3 to 10:11, 10:13 and 10:15 respectively. Hence, for 900 grams of the first stage resin, 178, 276 and 375 grams of p. xylylene dichloride would be needed to change the ratio to 10:11, 10:11 and 10:15 respectively.

TABLE 2

Flexural strength of R.A.7 and three terphenyl laminates of different ratios at room temperature after ageing at elevated temperatures

Hours	R.A.7	10:11	10:13	10:15
-	200°C	200°C	200°C	200°C
Nil	38,200 ±2,900	33,100 ± 9,400	24,600 ± 8,300	23,900 ±6,900
25	41,800 ±4,700	34,800 ± 4,400	31,400 ±10,400	28,200 ±4,200
50	42,300 ±5,000	34,100 ± 7,500	-	-
100	40,800 ±3,600	35,500 ± 6,300	28,200 ± 7,300	28,200 ±3,800
250	34,400 ±1,500	32,900 ± 1,500	28,100 ± 8,700	28,100 ±3,700
500	41,500 ±6,000	30,600 ± 6,300	26,900 ± 6,000	-
1000	26,600 ±2,000	39,800 ± 800	24,100 ± 9,600	28,300 ±2,300
2000	16,300 ±1,500	36,400 ± 8,600	22,700 ± 8,100	22,500 ±4,600
4000	< 3000	30,900 ± 5,900	20,200 ±11,000	17,300 ±3,500
-	230-240°C	230-240°C	240°C	240°C
Nil	38,200 ±2,900	23,000 ± 6,400	24,600 ± 8,300	23,900 ±6,900
25	44,800 ±6,400	27,000 ± 3,100	29,400 ±10,400	28,400 ±3,800
50	36,100 ±4,000	30,100 ± 3,900	-	-
100	26,000 ±1,700	27,000 ± 5,400	31,100 ±10,000	23,200 ±5,500
250	17,700 ±2,700	26,700 ± 8,600	27,300 ± 8,200	21,300 ±3,500
500	18,600 ± 800	26,700 ± 6,400	28,400 ± 7,500	-
1000	10,700 ±6,900	26,700 ± 9,100	22,400 ± 6,700	23,500 ±3,100
1500	7,900 ±1,800	-	20,300 ±10,700	17,900 ±8,100
2000	6,500 ±1,800	23,300 ± 7,300	10,800 ± 3,700	10,900 ±4,800
-	300°C	300°C	300°C	300°C
Nil	38,200 ±2,900	22,700 ± 5,900	24,600 ± 8,300	23,900 ±6,900
5	33,000 ±4,100	27,500 ± 8,500	19,900 2,300	25,800 ±3,800
10	38,200 ±3,100	-	-	-
15	25,700 ±5,600	27,500 ±10,000	26,000 ± 2,600	24,100 ±4,800
25	< 3000	22,600 ± 4,600	21,300 ± 9,500	25,100 ±1,500
50		18,200 ± 4,700	-	-
75		15,100 ± 7,400	15,200 ± 2,500	12,200 ±5,500
150		5,600 ± 900	< 3000	< 3000

TABLE 3

Flexural strength of R.A.7 and three terphenyl laminates of different ratios at elevated temperatures after ageing at that temperature

Hours	R.A.7	10:11	10:13	10:15
	200°C	200°C	200°C	200°C
1	36,100 ± 7,900	11,800 ± 7,200	12,550 ±3050	14,400 ±3,300
25	40,000 ± 3,800	13,200 ± 8,200	12,550 ±3000	21,600 ±3,600
50	39,100 ± 2,700	15,350 ± 8,650	-	-
100	34,100 ± 4,300	20,350 ± 8,850	13,500 ±4,600	22,100 ±3,100
250	33,300 ± 2,100	18,900 ± 3,900	17,800 ±5,100	19,500 ±4,100
500	40,100 ± 7,600	25,000 ± 9,900	13,800 ±1,200	20,600 ±4,100
1000	25,800 ± 3,000	31,000 ± 8,000	15,900 ±1,500	21,700 ±4,200
2000	16,100 ± 1,800	39,350 ± 6,650	17,000 ±1,200	23,000 ±3,700
4000	< 3000	25,600 ± 4,800	16,600 ±3,200	17,400 ±1,500
	230-240°C	230-240°C	240°C	240°C
1	40,600 ± 3,400	13,400 ± 4,500	8,900 ±3,500	11,900 ±4,200
25	39,200 ±10,300	18,300 ± 6,000	9,650 ±4,050	16,800 ±3,000
50	34,600 ± 5,400	23,200 ± 3,400	-	-
100	24,500 ± 4,500	22,100 ± 6,000	10,400 ±3,500	15,500 ±2,100
250	15,300 ± 2,100	21,900 ± 4,300	13,900 ±6,500	16,900 ±1,600
500	15,100 ± 1,600	-	14,100 ±3,600	20,100 ±2,000
1000	8,800 ± 2,900	23,200 ± 8,000	12,600 ±4,000	18,800 ±2,600
1500	6,000 ± 1,000	-	12,500 ±2,800	11,800 ±2,900
2000	-	19,800 ± 4,200	7,500 ±2,200	8,400 ±3,500
	300°C	300°C	300°C	300°C
1	38,800 ± 2,700	10,300 ±21,500	8,200 ±5,000	13,450 ±5,150
5	36,200 ± 4,300	11,700 ± 4,800	6,350 ±3,400	11,400 ±5,400
10	32,700 ± 1,500	-	-	-
15	25,700 ± 2,700	14,900 ± 6,300	7,350 ±2,700	9,600 ±3,500
25	< 3000	15,800 ± 6,800	7,200 ±3,300	10,500 ±2,600
50		17,700 ± 7,000	-	-
75		16,400 ± 2,900	6,000 ± 800	9,000 ±1,700
150		7,600 ± 2,900	< 3000	< 3000

TABLE 4

Density (grams/c.c.) and resin content of asbestos laminates bonded with terphenyl resins in three different ratios

		Density grms/c.c.			Resin content %		
Temperature	Hours	10:11	10:13	10:15	10:11	10:13	10:15
200°C	Nil	1·48	1·49	1·49	49·5	49·5	49·5
	250	1·48	1·52	1·49	47·7	50·0	51·0
	1000	1·49	1·48	1·51	48·0	50·5	53·0
	2000	1·49	1·53	1·53	47·4	47·5	52·5
	4000	1·52	1·55	1·49	44·4	49·5	
230*-240°C	Nil	1·43	1·49	1·49	46·8	49·5	49·5
	250	1·46	1·49	1·48	47·8	49·5	48·5
	1000	1·47	1·52	1·48	45·0	44·0	45·0
	2000	1·47	1·41	1·39	39·2	37·5	41·0
	4000	-	1·29		-	35·0	31·0
300°C	Nil	1·38	1·49	1·49	48·4	49·5	49·5
	50	1·37	1·45	1·46	44·2	44·2	45·2
	75	-	1·31	1·34	-	39·0	42·5
	150	1·28	-	1·06	31·7	-	24·0

*<u>Note</u>:- The 10:13 and 10:15 were aged at 240°C, whereas the 10:11 were aged at 230-240°C.

TABLE 5

Flexural strength of 10:11 ratio terphenyl/asbestos laminates after immersion in 40% solution of strong alkali

Hours exposure	Sodium hydroxide room temp.	Potassium hydroxide room temp.	Sodium hydroxide at 50°C	Potassium hydroxide at 50°C
Nil	36,500 p.s.i. ± 4,900			
100	32,900 ±3,300	29,600 ±1,200	26,900 ±1,900	26,800 ±400
500	37,300 ±3,500	32,500 ±9,400	29,400 ±2,800	34,700 ±1,400
1000	34,500 ±3,200	34,800 ±2,600	29,300 ±2,700	30,200 ±1,000
2000	28,900 ±1,600	28,700 ±5,700	29,800 ±3,800	27,900 ±1,200
4000	27,000 ±300	29,800 ±2,400	31,800 ±1,500	27,900 ±560

TABLE 6

Flexural strength of 10:11 ratio terphenyl/asbestos laminates after exposure to gamma radiation, tested at room temperature and at 240°C

Dosage	Room temperature	240°C
Nil	26,700 ±4,700	17,000 ±2,500
10 megarad	26,700 ±4,000	23,200 ±900
100 "	28,000 ±1,700	23,700 ±1,800
500 "	27,000 ±1,700	24,000 ±1,400

TABLE 7

Flexural strength of 10:11 ratio terphenyl/glass laminates after ageing at 240°C

Cloth finish	701		717		NOL-24	
Hours at 240°C	R.T.	240°C	R.T.	240°C	R.T.	240°C
Nil	39,200 ±3,000	-	46,400 ±2,000	-	50,100 ±7,100	-
5	-	17,900 ±1,800	-	20,500 ±5,900	-	10,100 ± 4,100
100	38,200 ±4,300	34,100 ±5,500	40,600 ± 900	28,300 ±4,900	44,400 ±6,900	25,700 ± 6,300
288	32,300 ±1,900	39,300 ±1,200	35,500 ±4,000	36,800 ±4,500	40,100 ±8,100	28,000 ± 8,700
500	-	37,400 ±1,700	-	34,500 ±2,400	-	29,300 ±12,300
1000	-	24,300 ±300	-	26,200 ±2,200	-	29,900 ± 3,200

TABLE 8

Percentage weight loss of 10:11 ratio terphenyl/glass laminates at 240°C, with the initial density and resin content

Hours at 240°C	701	717	NOL 24
100	+0·60	+0·35	+0·51
168	+0·51	+0·32	+0·60
288	+0·07	-0·02	+0·49
504	-0·89	-0·76	+0·07
1000	-3·61	-3·16	-1·98
Initial density	1·61 grms/cc	1·59 grms/cc	1·59 grms/cc
Initial resin content	30·3%	31·2%	28·6%

FIG. I.

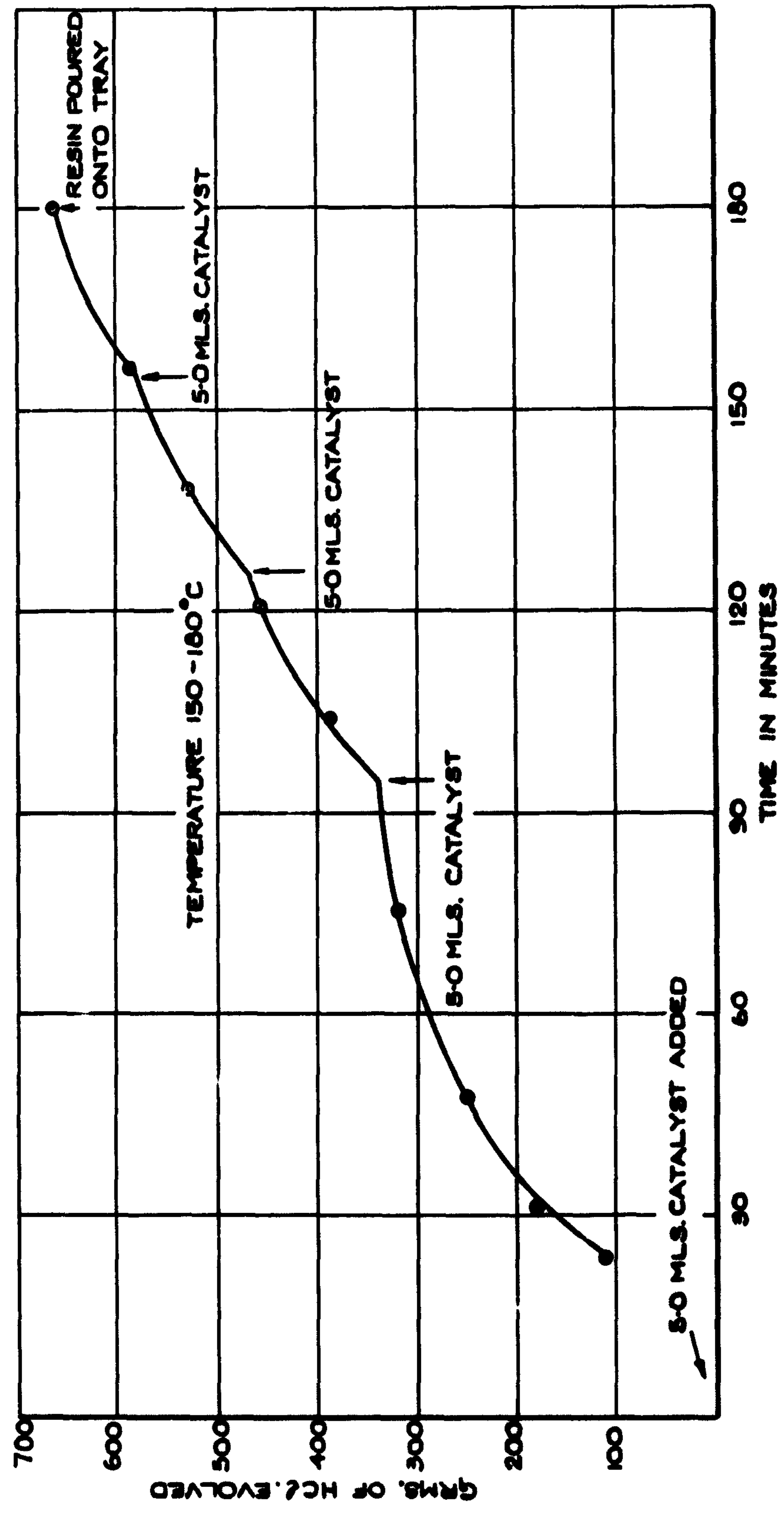

FIG. I. FIRST STAGE RESIN-LOSS ON HYDROGEN CHLORIDE AGAINST TIME.

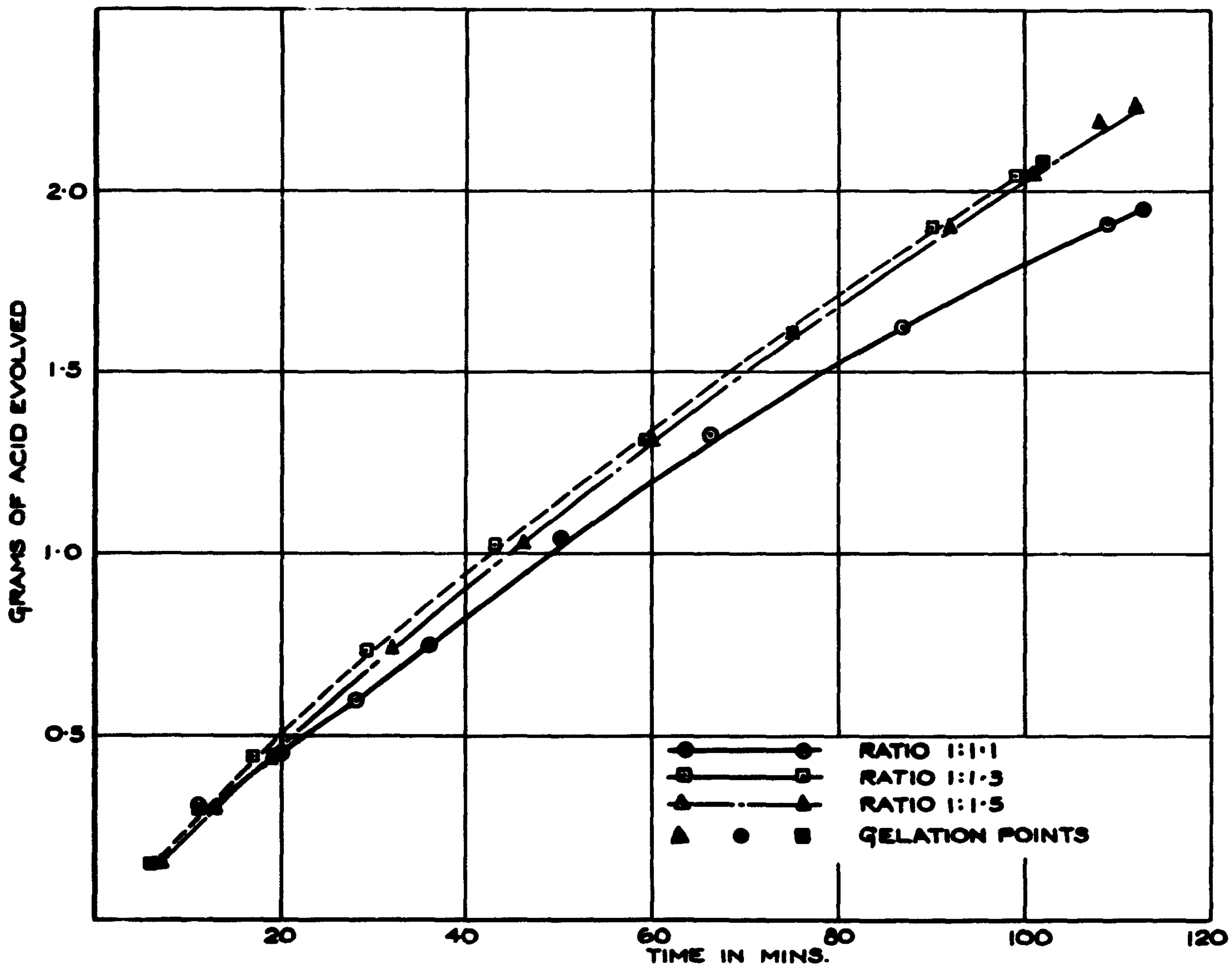

FIG. 2. SECOND STAGE RESIN–EVOLUTION OF HYDROGEN CHLORIDE TO GELATION.

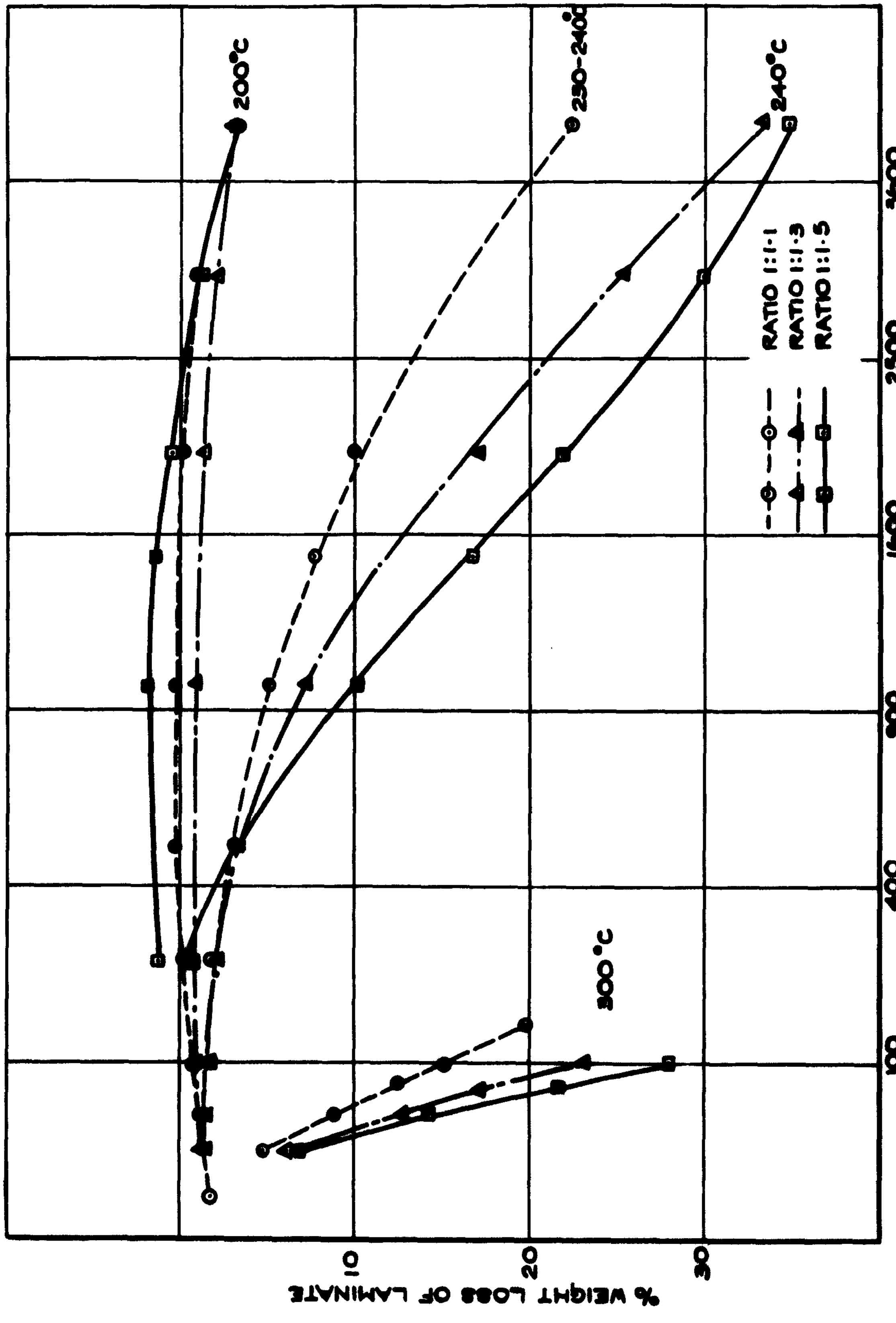

FIG.3. WEIGHT LOSS OF ASBESTOS LAMINATES BONDED WITH TERPHENYL RESINS.

FIG. 4.

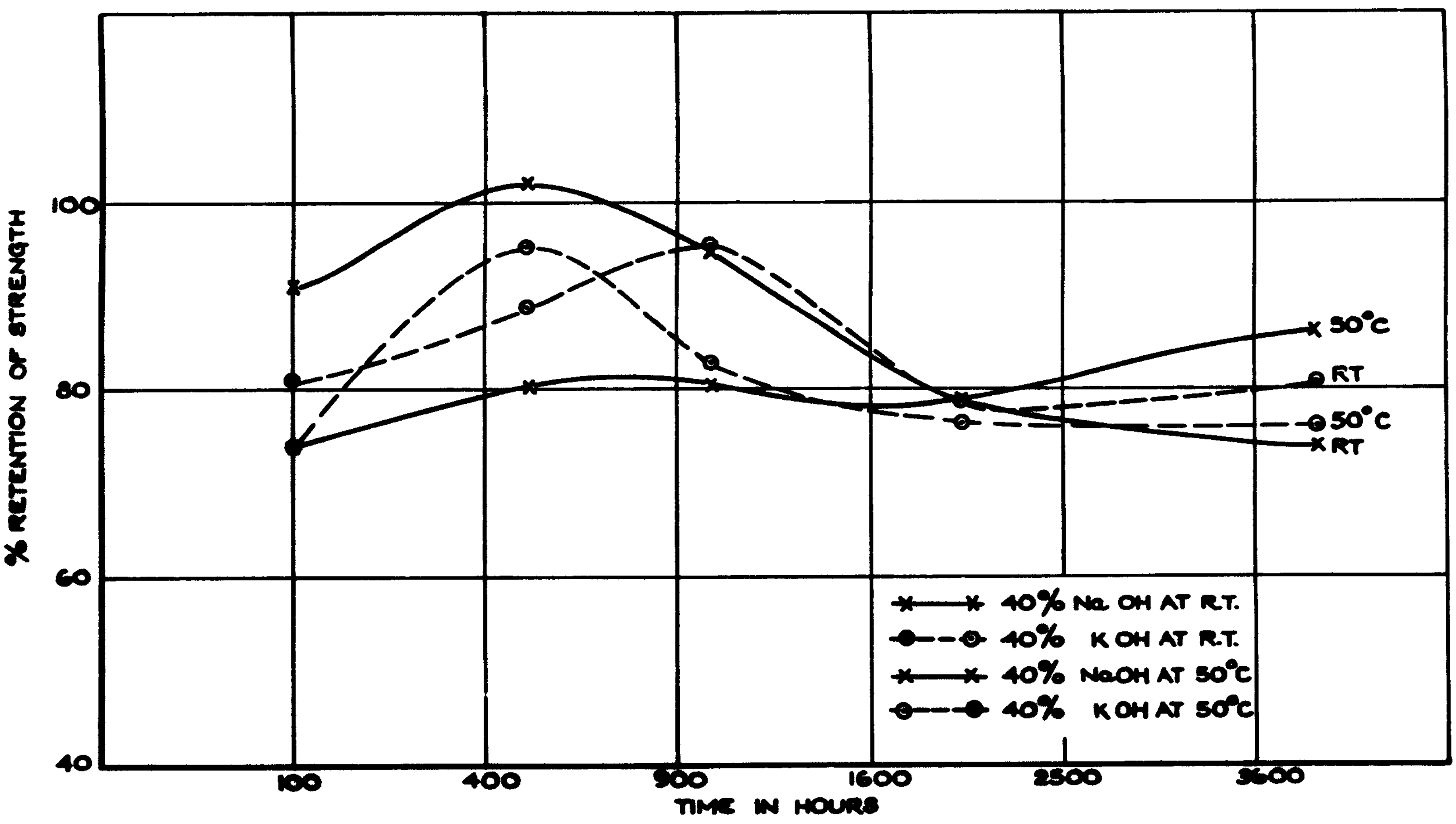

FIG. 4. PERCENTAGE RETENTION OF FLEXURAL STRENGTH OF TERPHENYL LAMINATES AFTER AGEING IN STRONG ALKALI.

FIG. 5.

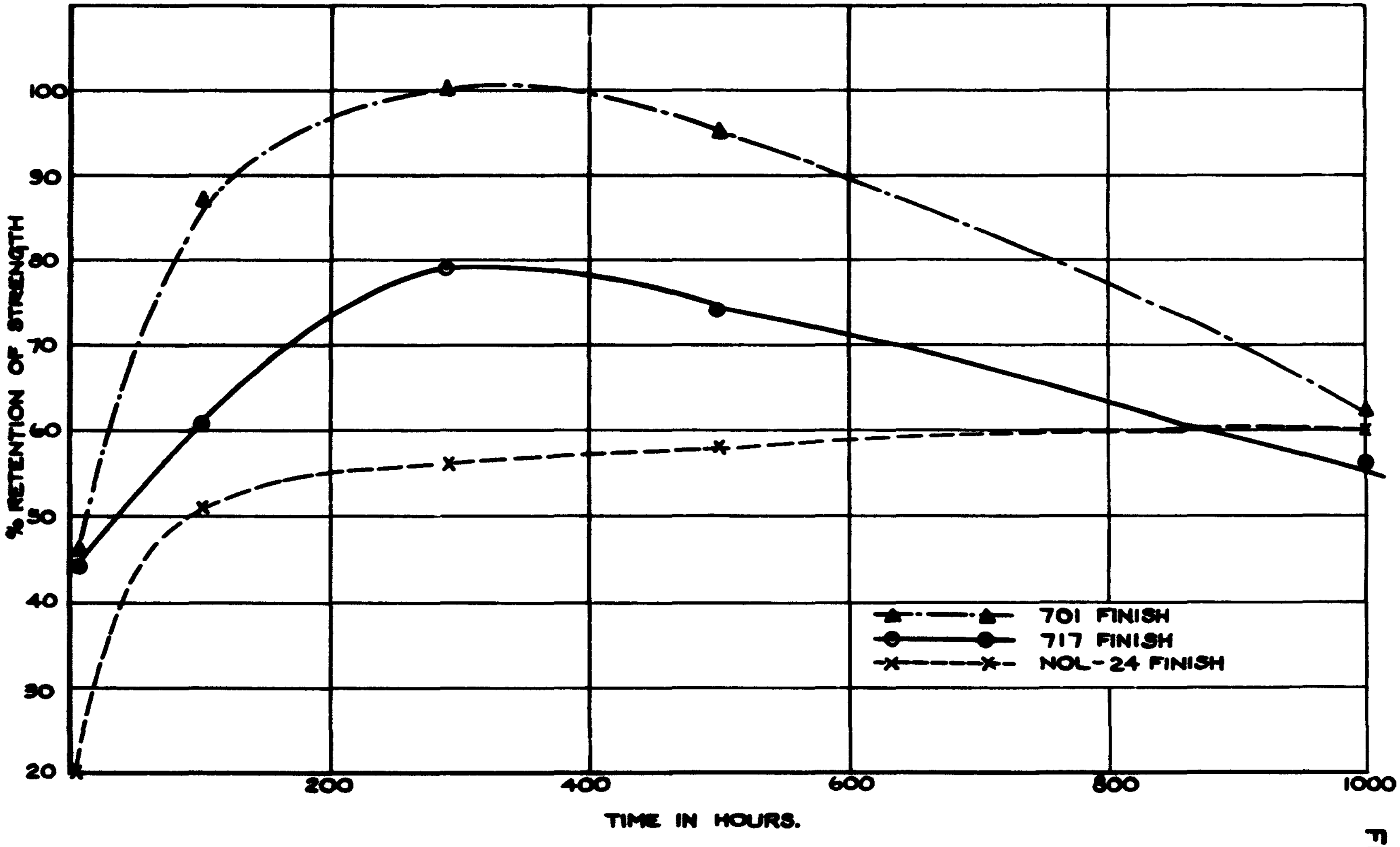

FIG. 5. PERCENTAGE RETENTION OF FLEXURAL STRENGTH OF TERPHENYL GLASS LAMINATES TESTED ON 240°C.

FIG. 6.(a – c)

INFRARED SPECTRA

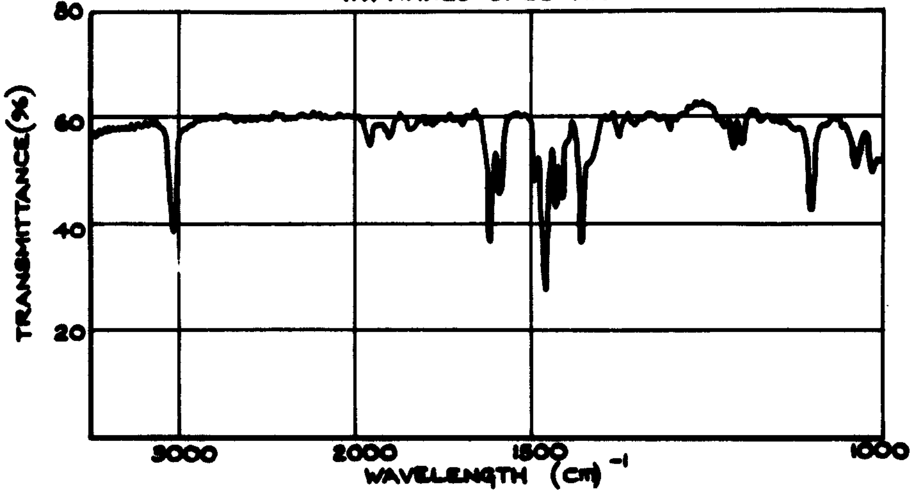

FIG. 6.(a) SANTOWAX R.

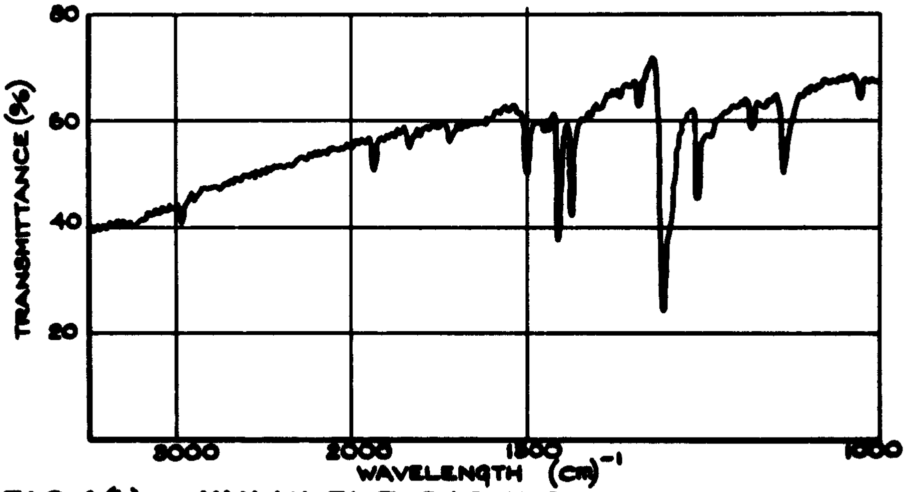

FIG. 6.(b) p. XYLYLENE DICHLORIDE IN K Br. DISC.

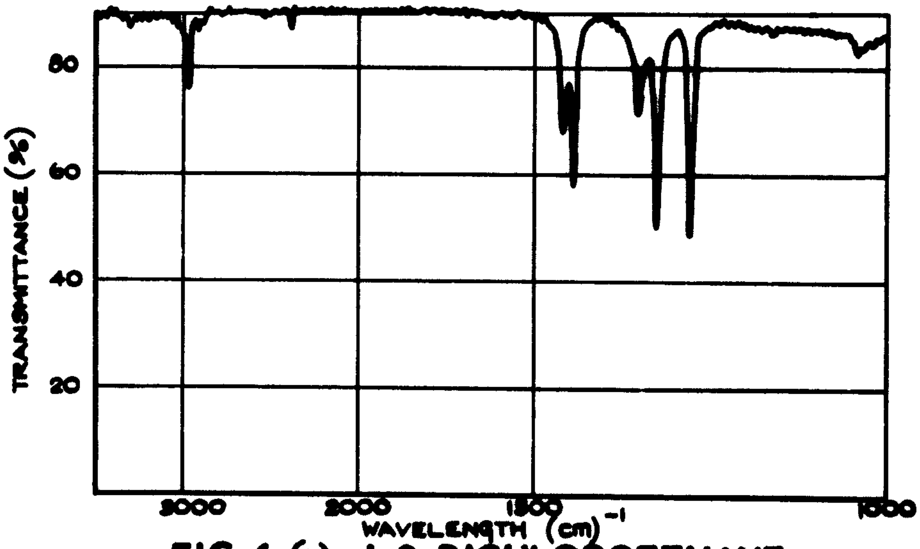

FIG. 6. (c). 1. 2. DICHLOROETHANE.

INFRARED SPECTRA

FIG. 7.(a – c)

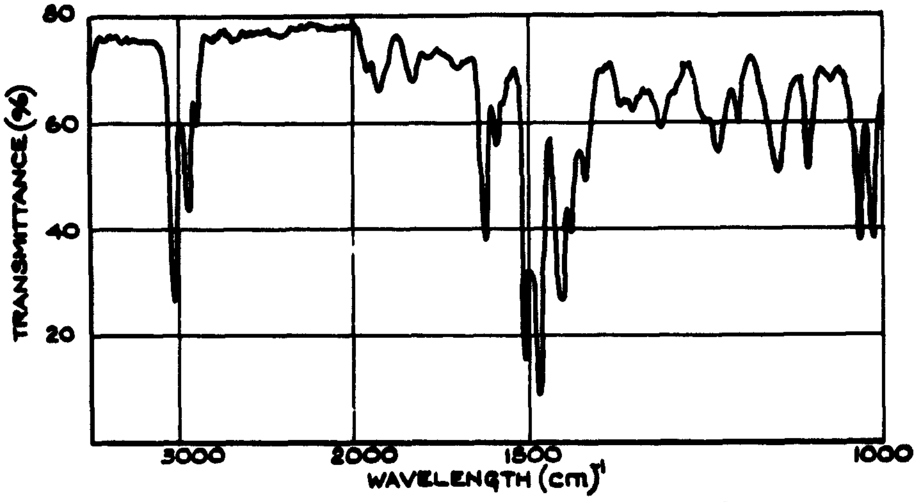

FIG. 7.(a) INITIAL TERPHENYL RESIN.

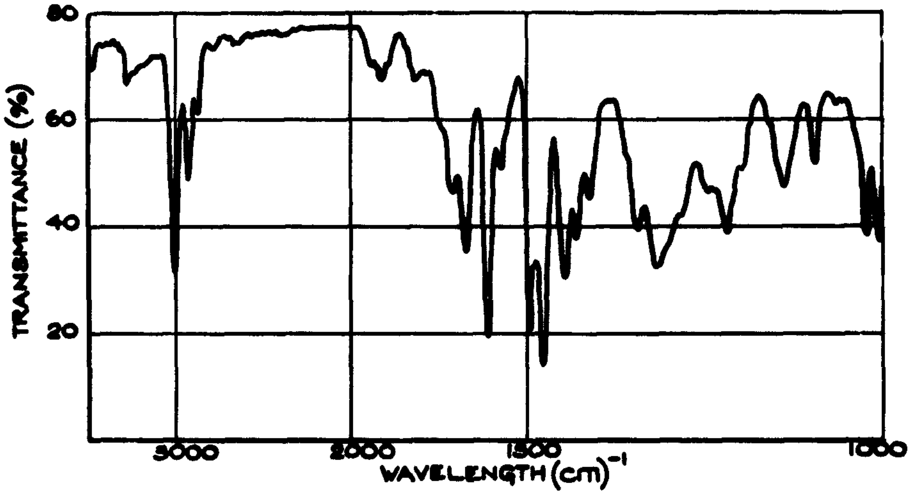

FIG. 7.(b) TERPHENYL RESIN AFTER 1 HOUR AT 185°C.

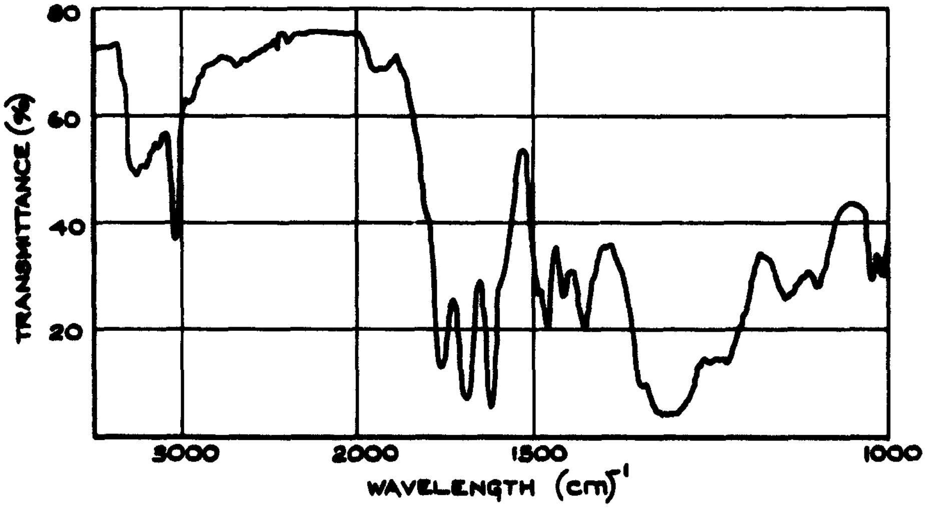

FIG. 7.(c) TERPHENYL RESIN AFTER FURTHER HOUR AT 300°C

INFRARED SPECTRA

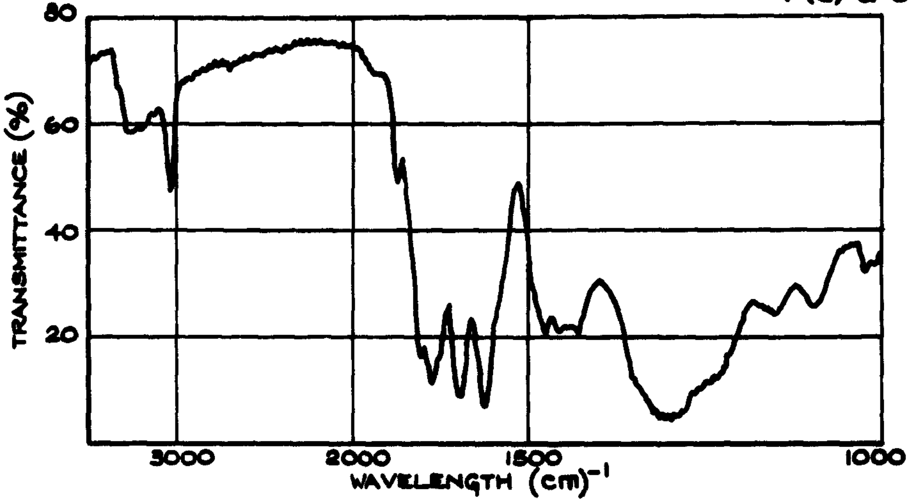

FIG.7(d). TERPHENYL RESIN AFTER PROLONGED EXPOSURE TO 350°C.

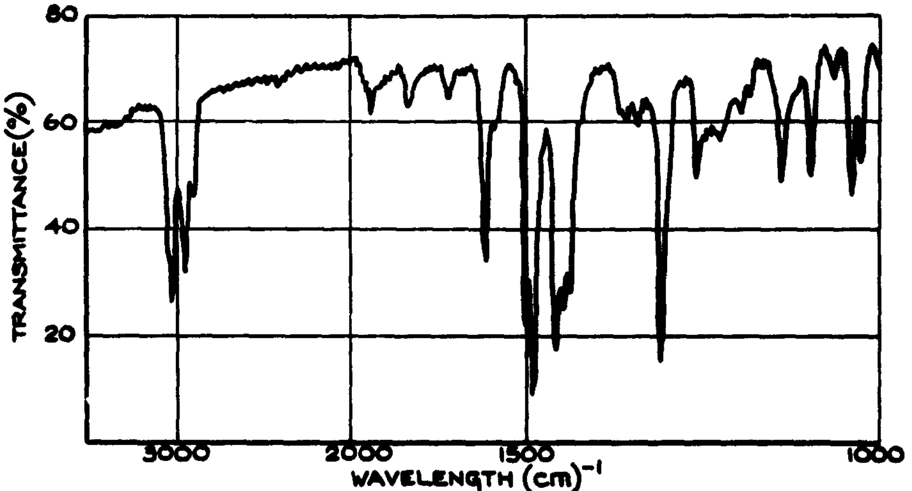

FIG. 8.(a). INITIAL POLYBENZYL RESIN.

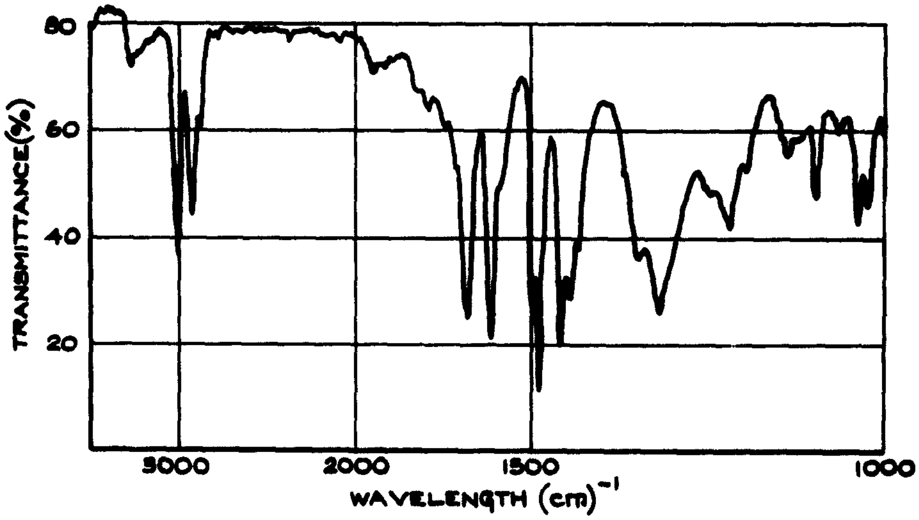

FIG.8.(b). POLYBENZYL RESIN AFTER 1 HOUR AT 185°C.

INFRARED SPECTRA

FIG 8.(c & d) & 9.

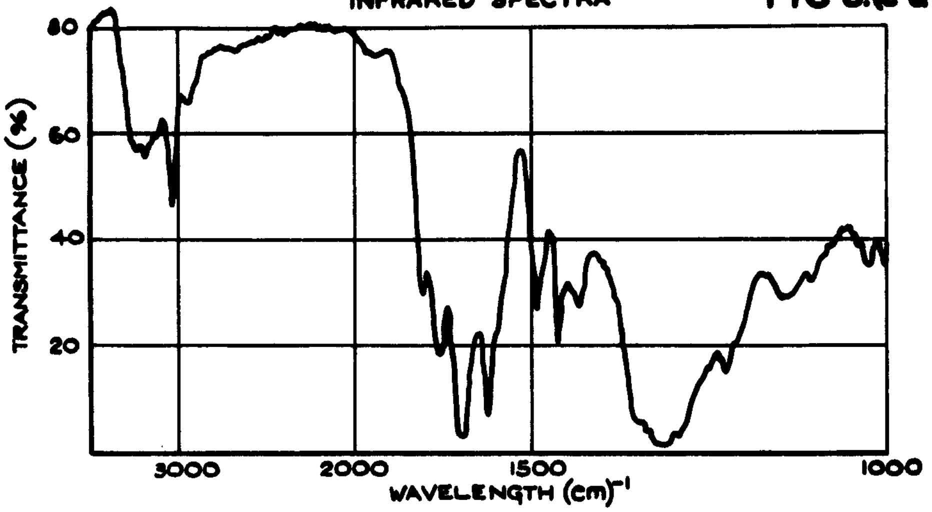

FIG. 8.(c) POLYBENZYL RESIN AFTER FURTHER HOUR AT 300°C

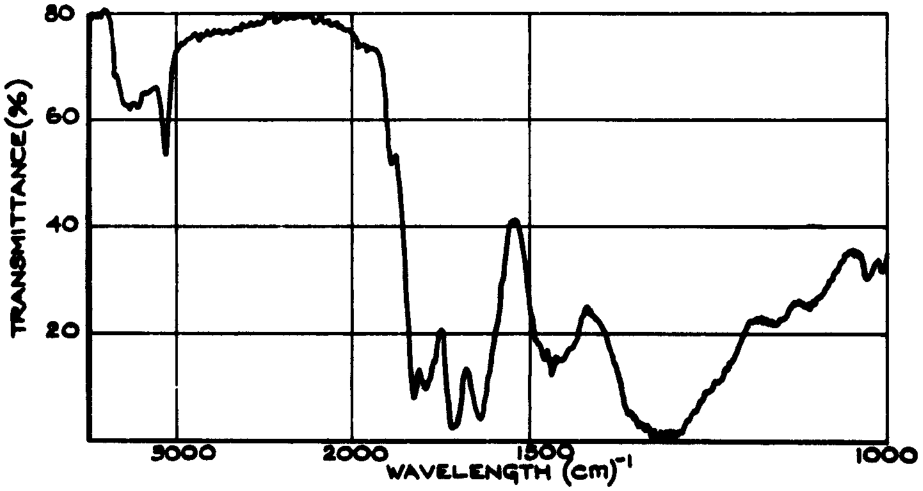

FIG. 8.(d) POLYBENZYL RESIN AFTER PROLONGED EXPOSURE TO 300°C

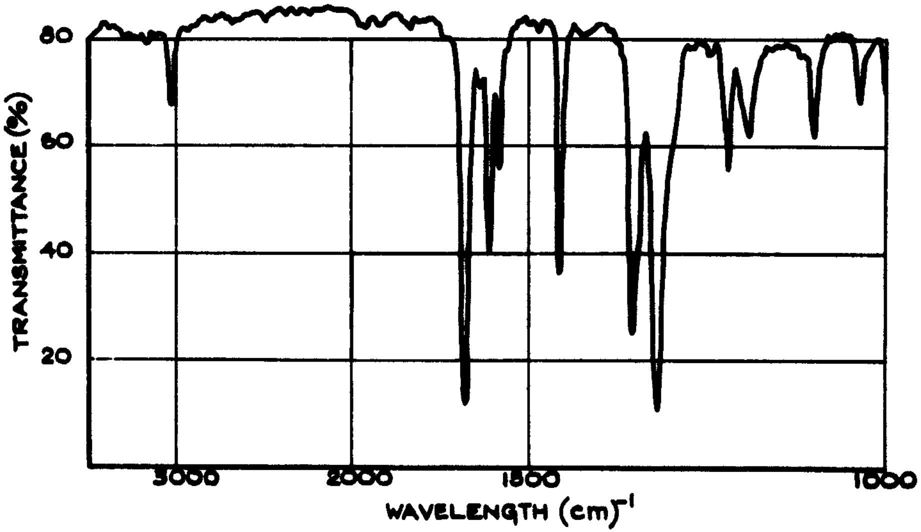

FIG. 9. BENZOPHENONE.

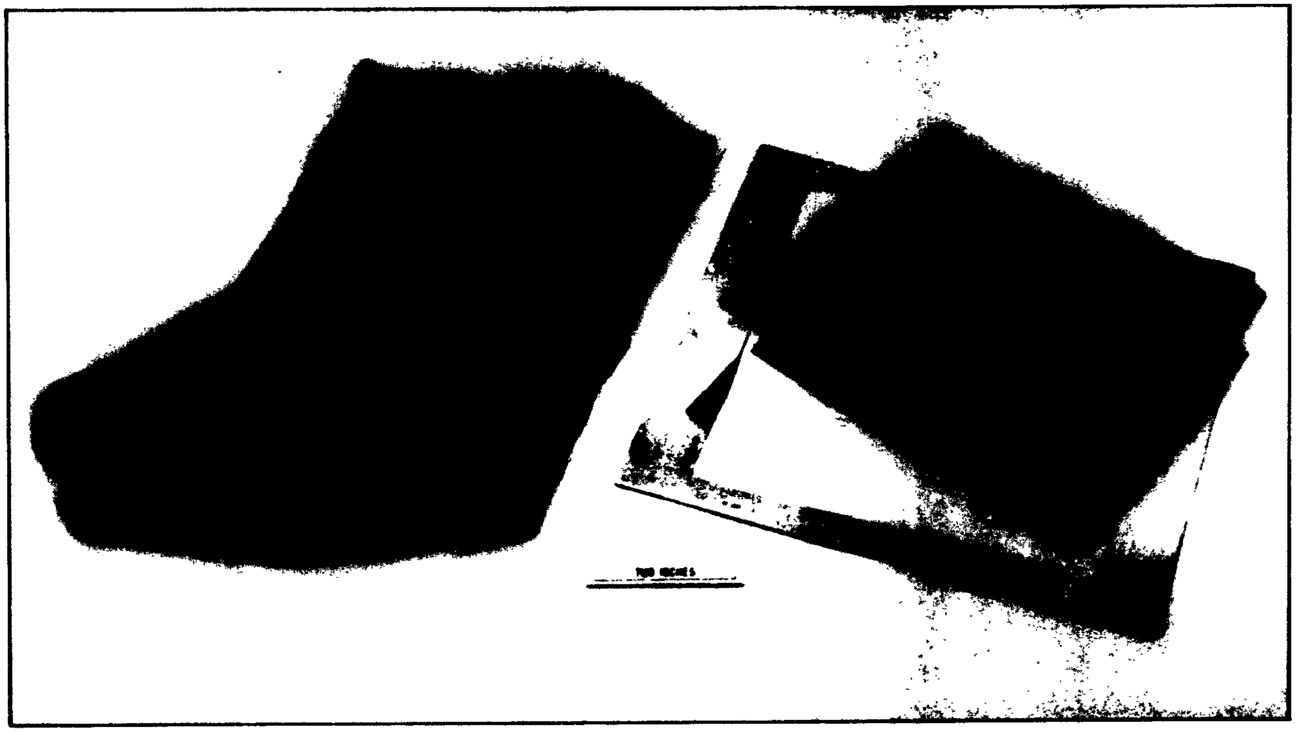

FIG.10. A RESIN IMPREGNATED GLASS CLOTH, LAMINATE AND FRAME MOULD

R.A.E. 164934 63

R.A.E: 164035 63

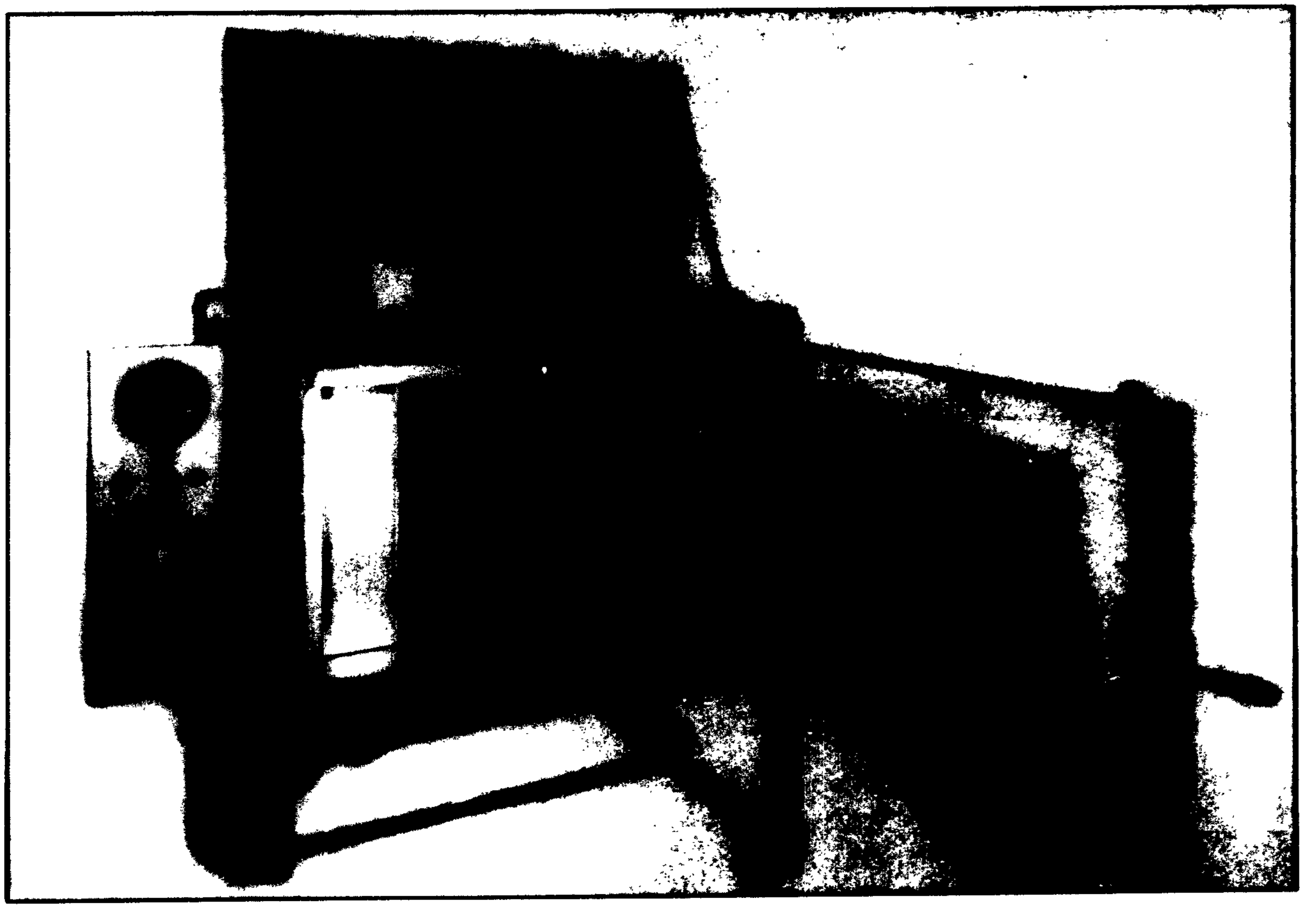

FIG.11. GENERAL VIEW OF HIGH TEMPERATURE FLEXURAL RIG

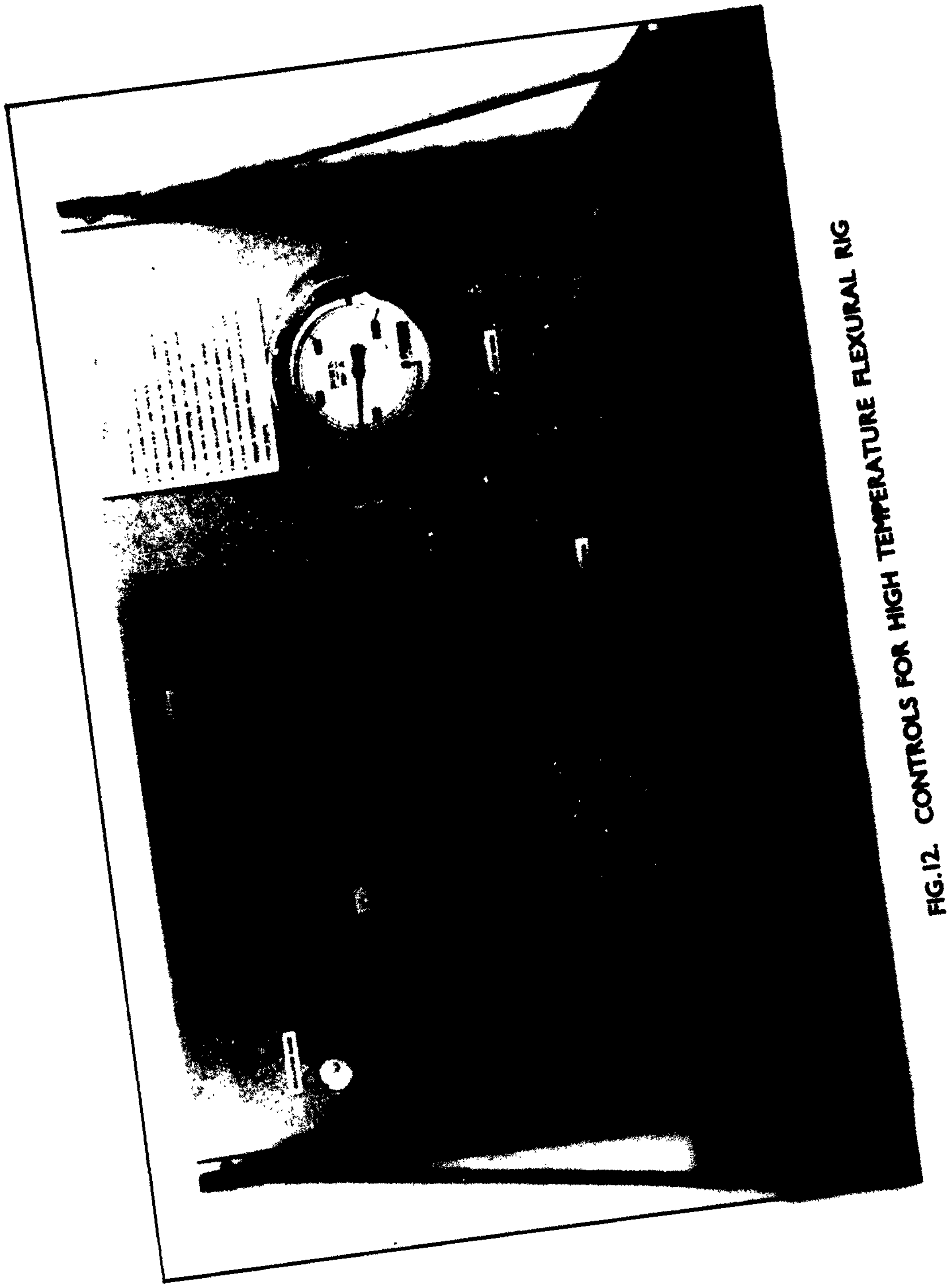

FIG.12. CONTROLS FOR HIGH TEMPERATURE FLEXURAL RIG

R.A.E. [illegible] 63

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Royal Aircraft Establishment 678.5-419

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Nixon, B. December 1963.

The production of heat resistant thermosetting resins based on terphenyl and p. xylylene dichloride in various ratios is described. The strength of the laminates made from these resins is shown not to differ greatly and it is concluded that the cross-linking density remains the same for the three ratios investigated.

The resistance of asbestos laminates to gamma radiation and strong alkali is investigated, together with some preliminary strength tests on glass reinforced laminates.

Infrared spectrophotometry shows that the methylene groups within both terphenyl and polybenzyl resins are oxidised during ageing at elevated temperatures.

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