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THE EFFECT OF CURING CONDITIONS ON THE EXTENT OF CURE OF POLYESTER RESIN CRYSTIC 189 (SCOT-BADER LTD.)

by

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SUMMARY

The cross-linking, or cure, of Scot Bader Polyester Resin Crystic 189 (L.V.) was investigated by examining the resin during cure by means of acetone Soxhlet extractions and Barcol hardness tests. The experiments were designed to test Funke's hypothesis that in the cure of polyester resins the nature of the final network is predetermined by conditions before the gel point, and that post-gel conditions affect the rate of cure but not the nature of the final network and the final degree of conversion. Funke's work was based on analysis of the final products of hydrolytic degradation of polyesters, which is quite different from the methods used in this investigation. It was concluded that the evidence did not support Funke's hypothesis and explanations are afforded for this and suggestions for future work are recorded.

Contents

Introduction

It is well known that the mechanical, electrical and chemical properties of polyester resins are sensitive to the degree of cross-linking of the material. In view of the increasing use of these materials in large structures, such as boats, which cannot be post-cured at elevated temperatures, it is desirable to have a method of assessing resin cure in a given time. It is also desirable to know whether room temperature cure ever gives complete cross-linking, and what effect on practical properties any lack of cure may have.

Historical Survey

This problem has been examined by Sub-committee 2 of the Joint Services Research and Development Committee on Plastics whose findings have been published[1, 2]. It was concluded that most of the physical methods examined could reveal gross undercure but were not capable of fine distinctions between fairly well-cured materials. The precision of the methods is masked by variations inherent in the polyester glass laminates examined, e.g. surface imperfections, overall and local variations in glass resin ratios, voids, etc. In general hardness (Barcol) gave a picture of degree of cure and also acetone extraction under carefully controlled conditions was a very useful method of following cure. It is unfortunately laborious and destroys the specimen. The techniques used to investigate cure of all thermosetting resins have been critically reviewed by Judd[3]. It is apparent from this review that no one method is sufficient alone, and any method must be related carefully to optimum physical properties. Detailed studies on the structure of cross-linked polyesters, including problems of cure, have been made by Funke[4,5], Funke, Roth and Hamann[6], Knodler, Funke and Hamann[7], and Feinauer, Funke and Hamann[8].

Cross-linked polyesters are subjected to totally destructive hydrolysis by caustic alkali and the residual compounds are analysed by chemical methods including elemental analysis, infra-red spectroscopy and viscosity measurements. The residual compounds are essentially maleate or fumarate residues linked to styrene units and the analysis gives the amount of styrene bonded into such compounds. Assuming hydrolytic scission is only at the ester groupds one may calculate the styrene in the original networks. By following the cauce of cure it was found that after the gel point the type of compound did not change, but that the yield increased with time and temperature. From this it was concluded that chemical processes up to the gel point predetermined the final degree of cure of the network. Changes of temperature after the gel point would only alter the rate of cross-linking, the final degree of cure and structure of the network having been already predetermined by conditions before gelation. If this were the case correct pre-gal conditions might ensure a resin giving optimum properties, where it would not be critical as to post-gel conditions. The main aim of the work reported in this Note is to test Funke's hypothesis.

The problem of assessing degree of cure in polyester resins is discussed in detail by Alt[9, 10, 11]. A sample of polyester/glass laminate powder is obtained by means of a cutter file clamped in a drill, the powder is extracted with methylene chloride and the methylene chloride extract is analysed for peroxides and for residual styrene using Wijs solution Glass content of the

powdered laminate is obtained by a separate pyrolysis experiment. It was shown that there is a relationship between the degree of cure of a polyester resin and its styrene content, but the relationship is not entirely unambiguous. The author claims however that his chemical analytical method has the advantage over other methods of being unaffected by glass fibre content. Determination of degree of cure by many physical properties, it is claimed, is greatly disturbed by the presence of glass fibres or fillers. Attempts were made to correlate degree of cure, determined chemically, with Martens temperature (a form of Heat Distortion Temperature). Certain resins, supposedly cured, acquired only 90-95% cure after two years, this kind of under-cure is more marked with resins having high Martens temperatures. The author concluded that polyester resins having a high heat distortion temperature must be extensively post-cured. Post-curing should be immediate, post-cure after two years did not have as great an effect as immediate post-curing. In other words a state of under-cure may set in which can be no longer eliminated. Alt also attempts to correlate degree of cure, measured by chemical analysis, with a number of physical properties such as hardness, flexural strength, tensile strength, mechanical loss factor, chemical resistance, water absorption and yellowing. It was noted also that there is more free styrene associated with amine cured systems, as compared with cobalt cure. Acetone extraction methods of following cure in polyesters are described by Wiegand and Wallhauser.[12]

A dilatometric method of assessing polyester cure is described by Perlin, Gilman and Leites.[13] The dilatometer described by these authors proved capable of showing degree of cure by measurement of shrinkage on cure. It was claimed that the method can distinguish between permanent incomplete cure and merely temporary incomplete cure. The work was done on cast resins and involves a fairly large specimen. Whether this method could be used for large, complete structures is doubtful.

Changes in attenuation and velocity of ultra-sonic waves during cross-linking of a polyester resin were investigated by Sofer and Hauser[14] as a means of following that process. These properties, especially attenuation, appeared very sensitive to the gel point, and could well be a means of following cure in unfilled materials, but due to numerous imperfections introduced by laminating it seems unlikely that ultrasonic methods would be useful in following cure in a polyester laminate. A considerable amount of work on changes of electrical resistivity of thermosetting resins, including polyesters, during cure has been done, the initial approach being by Fineman and Puddington.[15] The method has been further developed by Warfield and his co-workers. A special cell for measuring changes in specific resistivity during cure is described by Aukward, Warfield and Petree.[16] This method was used for cast, unfilled, polyester resin. A marked and useful change in specific resistivity with cure was observed and reasonable correlation with infra-red evidence was obtained. Similar work was reported by Aukward and Warfield.[17] Further work by Warfield and Petree[18] confirmed that electrical conduction in polymers is an ionic diffusion process controlled by an activation energy. They stated also that the technique is not self-sufficient and resistivity data must be compared with that obtained by other methods. Warfield and Kenna[19] report that using an epoxide resin, volume resisitivity changes may be used to monitor cure in a large reinforced ring structure, apparently with a degree of success. This has not yet been done, to the authors knowledge, on polyester reinforced structures, but these results may hold out some prospect of success for polyester laminates. Degree of cure in polyester dough moulding compounds is discussed by Tomkins[21] in terms of hot needle indentation tests.

Aims of the present work

If the hypothesis of Funke is correct the vital part of curing a polyester resin is that preceeding the gel point. During this period the nature of the network is being predetermined, after the gel point only the speed of reaching the final state is affected by external conditions. The work reported in this Note was designed to test the hypothesis by comparing the cure of resins cured up to the gel point under identical conditions, but after the gel point at different temperatures. The cure of the resins was followed by Barcol hardness tests and acetone Soxhlet extractions under standard conditions.

Experimental methods

All experiments were performed on Scot Bader Ltd. polyester resin Crystic 189 (L.V.), the catalyst and accelerator used were catalyst Paste H and Accelerator E. Resins gelled at 118°C contained neither catalyst nor accelerator, all other experiments were conducted with the following resin/catalyst formulation:-

Crystic 189	50g.
Paste H	0.5g.
Acc. E	2 mls.

Resin for experiments having gelation at 118°C was special deinhibited material, to facilitate thermally initiated cure.

Resin was mixed with catalyst and accelerator and poured into a boiling tube $5^3/_4'' \times {}^7/_8''$ which was placed in a water bath (or vapour bath for gelation at 118°C) at the temperature required up to the gel point. The gel time was estimated by means of a Techne gel timer. After the gel point had been reached the disc of the gel times was removed, and the boiling tube transferred to an oven at the required temperature. After one hour the casting was removed from the tube, a piece cut off, and the casting returned to the oven. At appropriate time intervals further pieces of resin were cut off for examination. After cooling to room temperature, the hardness of the cut pieces was measured using a Rockwell Barcol hardness tester, (average of eight readings throughout). The cut pieces were stored at - 15°C, rasped and subjected to acetone extraction using the Soxhlet extraction procedure described in Reference 2. Because the resins were unfilled a nominal 1g. of raspings was used in the acetone extractions, rather than the 2g. recommended for laminates. All rasping was done with a surform. Degree of cure was thus estimated (as a percentage extraction) as a function of time during cure beyond the gel point.

In separate identical experiments, using a thermocouple embedded in the resin, the actual temperature in the casting was measured. This will, in general, differ from the external surroundings due to the occurrence of exotherms on curing.

The pattern of experiments was as follows:-

Temperatures are external to the casting.

Temp. to gel point	Temp. after gel point	Code for experiment
20°C	20°C	20/20
20°C	40°C	20/40
20°C	60°C	20/60
40°C	40°C	40/40
40°C	60°C	40/60
40°C	80°C	40/80
60°C	60°C	60/60
60°C	80°C	60/80
60°C	100°C	60/100
118°C	120°C	118/120
118°C	140°C	118/140
118°C	160°C	118/160

Experimental results

The results of Barcol Hardness Tests during cure are set out in tabular form below. (Table 1). Owing to the round surface of the cut sections, and the rough nature of cut surfaces it is very doubtful whether these figures have much quantitative significance. A considerable scatter in hardness measurements was noted, and the author has doubts concerning their significance.

Time after gel.	Ex. 20/20	Ex. 20/40	Ex. 20/60	Ex. 40/40	Ex. 40/60	Ex. 40/80	Ex. 60/60	Ex. 60/80	Ex. 60/100	Ex. 118/120	Ex. 118/140	Ex. 118/160
1 hr.	0	31	25	0	19	18	16	9	-	0	-	10
2 hrs.	0	24	32	0	15	17	17	7	5	3	20	24
3 hrs.	0	26	25	-	20	24	15	12	7	3	-	22
4 hrs.	0	-	23	0	24	22	18	7	5	6	26	27
5 hrs.	0	23	-	-	-	-	-	7	-	-	-	-
6 hrs.	0	-	21	3	23	22	16	-	7	-	-	-
19-24 hrs.	0	31	36	23	25	30	23	27	23	15	-	23
48 hrs.	0	31	-	22	-	-	-	-	-	-	-	-
15 days	8	-	-	-	-	-	-	-	-	-	-	-

In Ex. 118/140 there was extreme difficulty in measuring hardness due to crazing in the castings.

The results on acetone Soxhlet extractions during cure are set out below in Table 2 and are expressed in graphical form in Figs. 1 - 12.

Table 2. Acetone Extractions

Time after gel.	Ex. 20/20	Ex. 20/40	Ex. 20/60	Ex. 40/40	Ex. 40/60	Ex. 40/80	Ex. 60/60	Ex. 60/80	Ex. 60/100	Ex. 118/120	Ex. 118/140	Ex. 118/160
1 hr.	-	7.9%	8.4%	22.8%	9.2%	9.9%	10.3%	-	10.2%	13.9%	8.4%	7.5%
2 hrs.	28.4%	8.1%	8.9%	17.8%	9.4%	10.0%	10.0%	10.0%	9.8%	11.0%	8.2%	7.6%
3 hrs.	-	9.0%	9.2%	-	9.4%	9.8%	10.1%	9.6%	-	10.1%	-	7.2%
4 hrs.	21.5%	-	9.9%	14.3%	9.9%	10.0%	10.5%	9.9%	9.6%	9.7%	7.0%	7.4%
5 hrs.	-	8.7%	-	-	-	-	-	9.9%	-	-	-	-
6 hrs.	18.7%	-	9.4%	13.7%	9.6%	9.8%	10.3%	-	9.3%	-	7.3%	-
19-24 hrs.	16.3%	8.5%	9.5%	11.5%	9.9%	9.1%	10.3%	9.2%	8.3%	7.8%	6.3%	4.7%
48 hrs.	15.1%	8.5%	-	10.5%	-	-	-	-	-	-	6.4%	-
15 days	12%	-	-	-	-	-	-	-	-	-	-	-

Figures 13-21 compare temperatures inside the castings with external temperatures, these obviously differ due to exothermic heat generated during cure. In general, exotherms exhaust themselves within an hour from the gel point, and the temperature of the casting is then substantially the same as its surroundings. Most peaks show a very rapid rise in temperature, followed by a fairly rapid descent, at least in the initial stages.

Interpretation of results

It is Funke's hypothesis that post-gel conditions in polyester cure only affect the rate of cure, but not the attainable final conversion and network structure.

Comparing Ex.'s 20/20, 20/40, and 20/60, the first has probably not levelled off in 15 days, the 20/40 ex. levels at approx. 8.5%, whereas the 20/60 ex. levels at approximately 9.4%. One would expect this to level to the same as the 20/40 ex. only more rapidly. Likewise comparing the Ex.'s 40/40, 40/60 and 40/80 the 40/40 does not level off, the 40/60 levels off at 9.6-9.9% but the 40/80 has not levelled off completely at 9.1%. One would expect the 40/80 ex. to level off more rapidly than the 40/60. Comparing ex.'s 60/60, 60/80, and 60/100 there is a marked early levelling off of the 60/60 ex., the 60/80 ex. is still curing and the 60/100 ex. is probably not levelled off completely at 8.3%. Within a set of cures having the same pre-gel conditions, but differing post-gel conditions one does not see a more rapid levelling to an extraction figure characteristic of the pre-gel temperature.

If one considers ex.'s 20/60, 40/60 and 60/60 (extraction figures 19-24 hours) these are much closer to each other (9.5%, 9.9%, 10.3%) than some of the figures within a set having the same pre-gel conditions e.g. ex.'s 60/80 and 60/100 at 9.2% and 8.3% respectively and where post-gel temperatures are high enough to give reasonable cure. Indeed ex.'s 40/80 and 60/80 give a similar comparison, though on the other hand ex.'s 20/40 and 40/40 certainly do not.

The graphs of internal temperatures of the castings show for the most part, a very rapid rise in temperature after gelation, but exotherm peaks are surprisingly sharp and indeed exothermic heat is normally dissipated within one hour of gelation under the experimental conditions used. It is possible that the network is affected by such elevated temperatures, enabling some rearrangement to take place, but on the other hand the elevated temperatures are not of long duration. In some instances, notably ex.'s 20/40, 20/60 and 40/60, the phenomenon of an initially upward rising curve was noted, for acetone extractions. Superficially this suggests materials become degraded ('less cured') after a period of time, and then proceed to cure again. A more likely explanation would seem to be that material which would normally be extracted is being lost by evaporation. During cure, in the early stages, much material (styrene) is volatile and not yet linked into the network. Exothermic heat may volatilise this. As gelation proceeds the 'sol' phase may be trapped by the 'gel' material and be no longer volatile, but still extractable by acetone. Under other conditions the 'gel' may trap the 'sol', volatile material very rapidly so that volatilisation does not occur, also in some cases there may be so much volatile material that the initial extraction figures are still descending.

In summing up it appears that the results do not give any conclusive support to Funke's hypothesis. In part this may be due to the fact that his approach to the problem is by entirely different methods. Two differing polyester networks could be hydrolysed down to maleate/fumarate residues linked by styrene, the mixture of compounds so obtained from differing networks could be isomeric and this would not easily be detected by elemental analysis, infra-red spectroscopy or viscosity measurements. Thus one might suppose two differing polyester networks were in fact the same. Also if exothermic heat, which is dependent upon geometry, does cause some rearrangement of the network near the gel point the pre-determination of the network by pre-gel conditions would be prevented. If this were so Funke's hypothesis would apply only under certain geometrical conditions i.e. those that did not lead to an appreciable exotherm.

Throughout the literature the term 'cure' is often used loosely. One may define absolute chemical cure as being the formation of cross-links between polymer chains such that a three-dimensional network is built-up. The cross-links that give unlinked side branches, or the formation of intra-molecular loops etc. do not constitute cure, though chemical analysis would not distinguish the type that gave network formation from that which did not. Cure may also be used more loosely in terms of the optimisation some physical property, in which case the point of full cure varies according to the property. In such cases the property should be stated clearly.

Suggestions for further work

Though Funke's hypothesis is of academic interest it does not appear to offer much help in solving the practical problem of assessing cure in large polyester/glass structures. Post-gel conditions would still seem to be of importance. The work of Alt[9, 10, 11] shows useful and practical results, depending on residual styrene and peroxide contents of resins, these being properties independent of the glass part of the laminate. Styrene is already estimated in the methylene chloride extracts by gas chromatograph, which may be easier than by the use of Wijs solution as Alt recommends. Possibly infra-red spectroscopy may also be used. Hopefully a correlation between styrene content of the extracts and refractive index of extracts may be used to facilitate quick estimation of styrene content. Much remains to be done to correlate residual styrene with physical properties.

The work of Kinna and Warfield[19] on the changes in specific resistivity of a filled epoxide ring structure also appears promising. To the author's knowledge this has not be done on glass-filled polyester structures. Much more knowledge would be needed concerning the effects of humidity, changes in glass-content and the nature of the glass, perhaps also the effects of added ions. Nevertheless small electrodes could easily be embedded in a laminated structure and relatively speedy tests made.

The majority of physical properties, as much experience shows, are not very sensitive or satisfactory methods of following cure, this kind of approach has been very well explored. It is also conceivable that pyrolytic degradation of a laminate (as only the polyester is affected) might reveal changes in pyrogram due to the curing process.

In our view the approaches of Alt, on residual styrene content, and Kinna and Warfield on volume resistivity represent the best avenues for future exploration.

Acknowledgements

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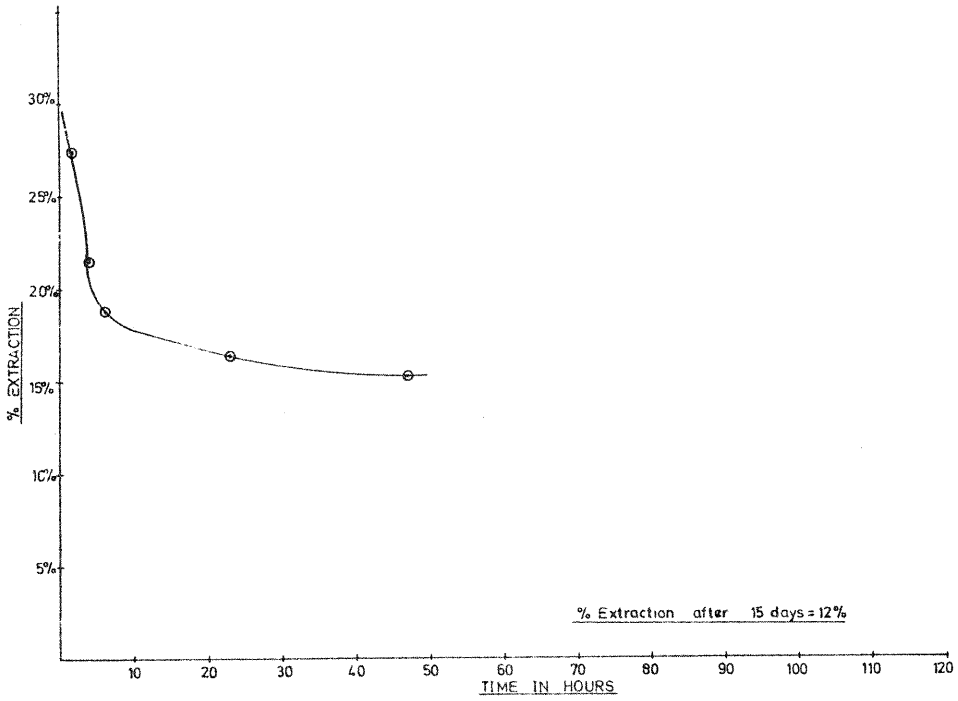

FIG 1 ACETONE EXTRACTION % EXTRACTION V TIME
EX 20/20

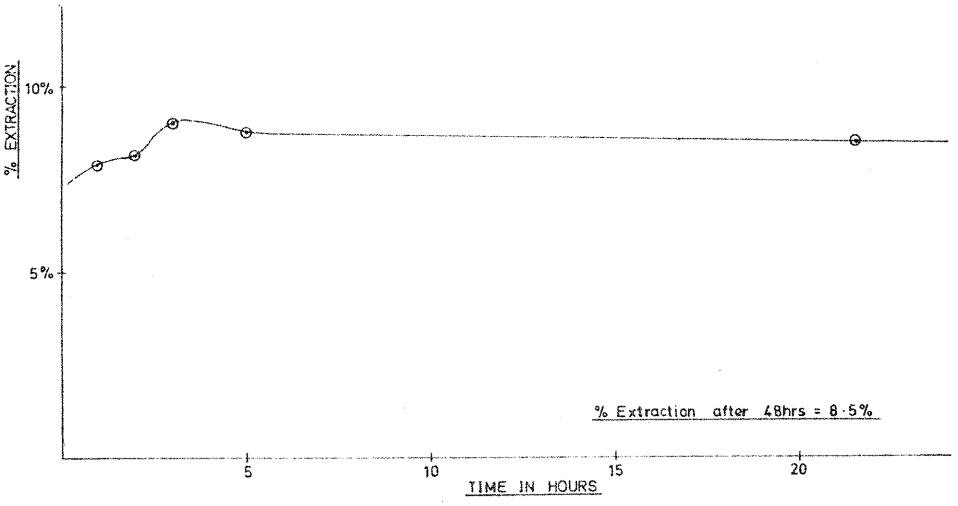

FIG. 2 ACETONE EXTRACTION % EXTRACTION V TIME
EX 20/40

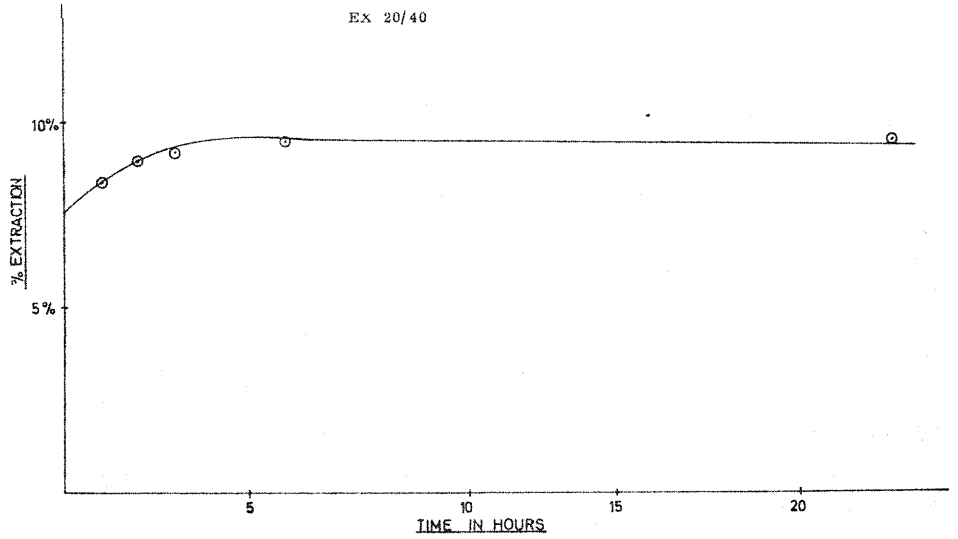

FIG. 3 ACETONE EXTRACTION % EXTRACTION V TIME
EX 20/60

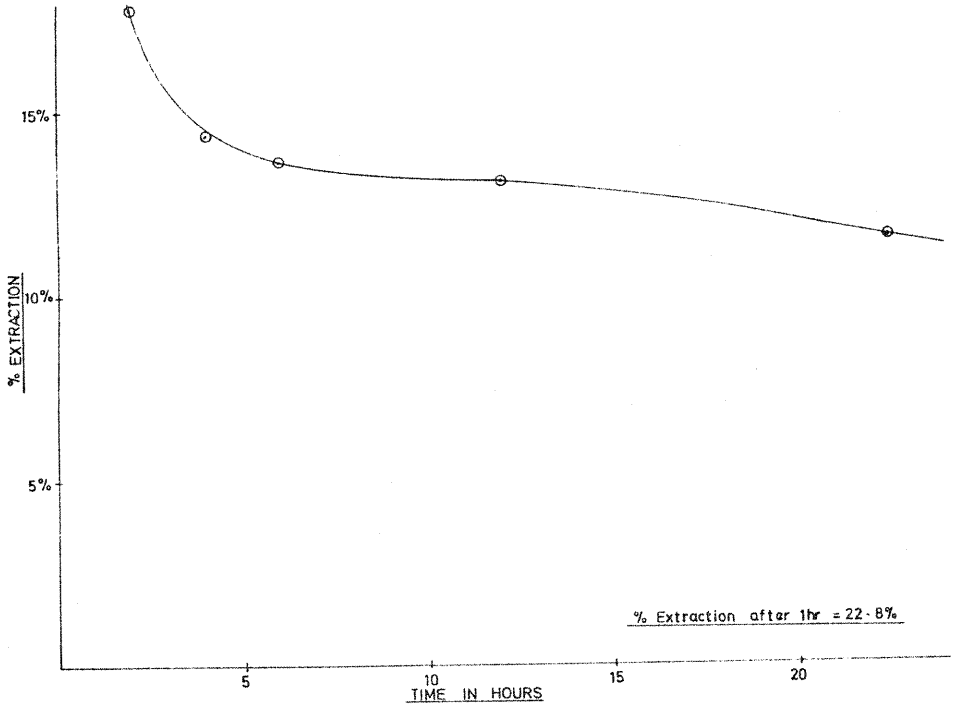

FIG. 4 ACETONE EXTRACTION % EXTRACTION V TIME
EX 40/40

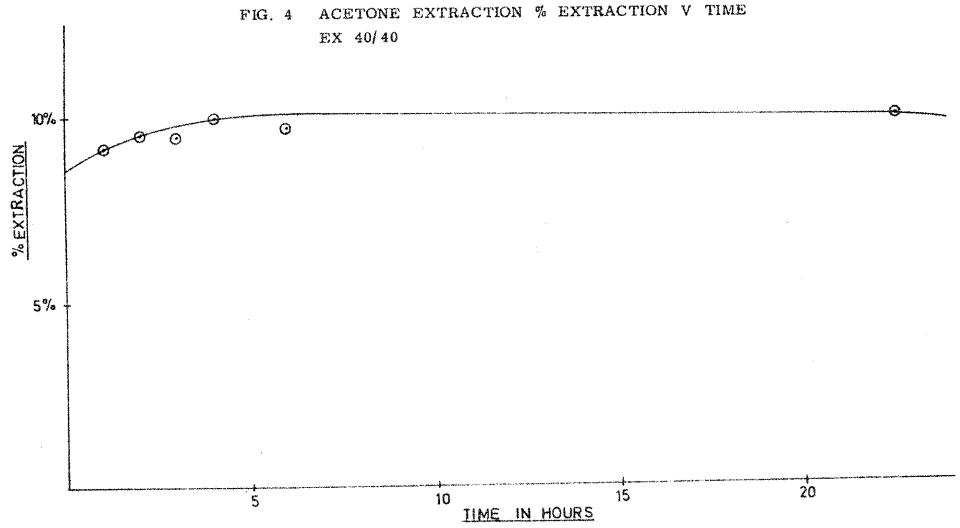

FIG. 5 ACETONE EXTRACTION % EXTRACTION V TIME
EX 40/60

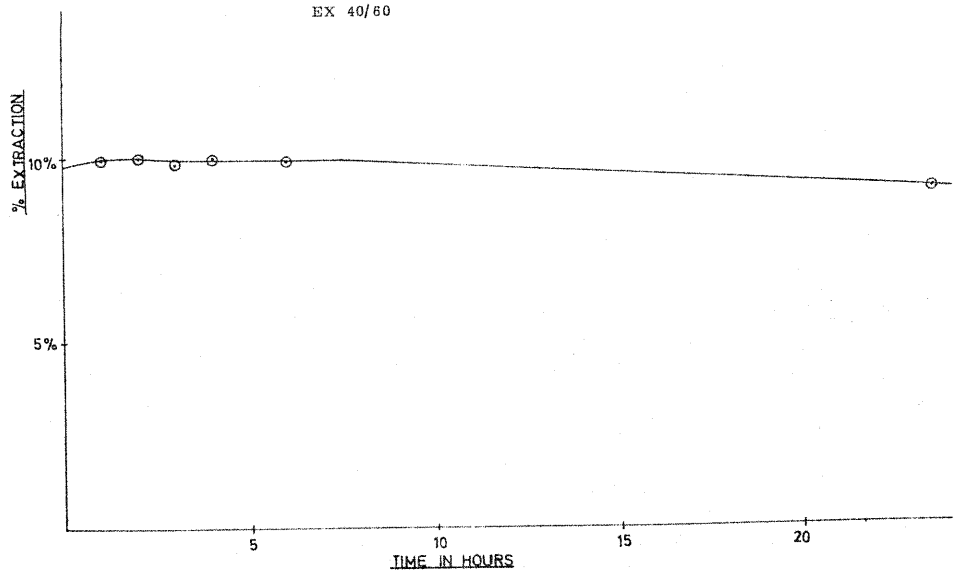

FIG. 6 ACETONE EXTRACTION % EXTRACTION V TIME
EX 40/80

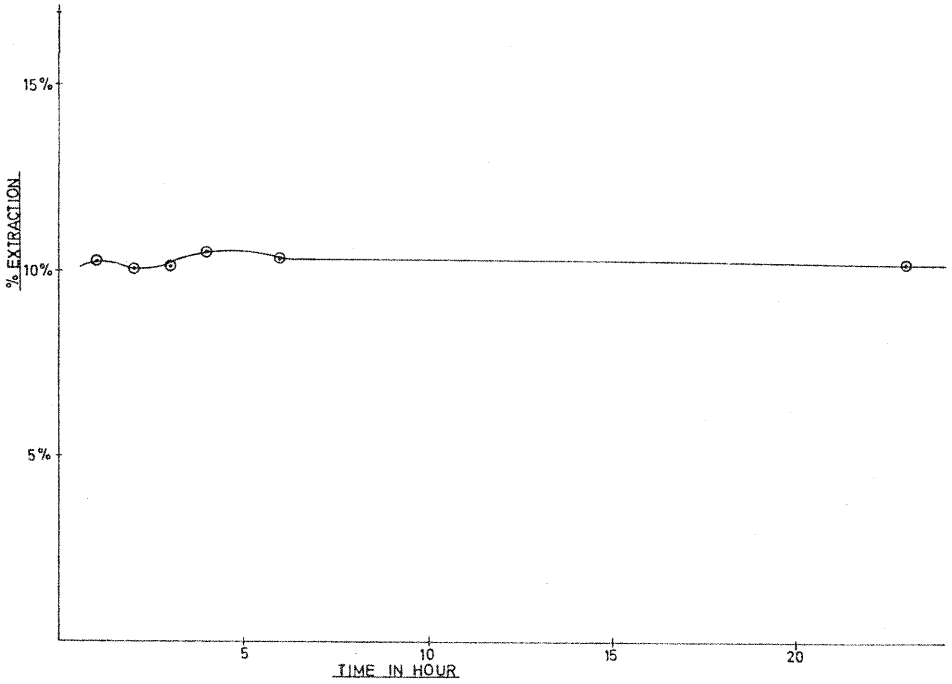

FIG. 7 ACETONE EXTRACTION % EXTRACTION V TIME
EX 60/60

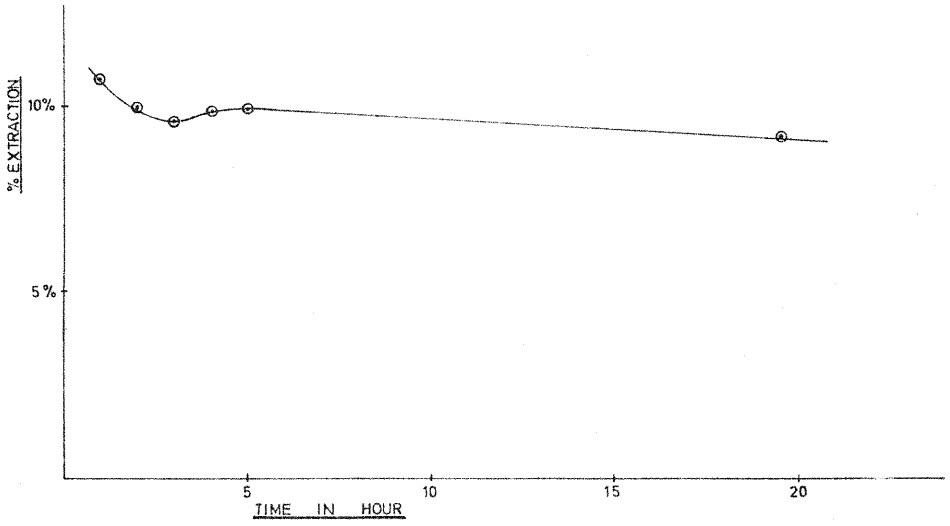

FIG. 8 ACETONE EXTRACTION % EXTRACTION V TIME
EX 60/80

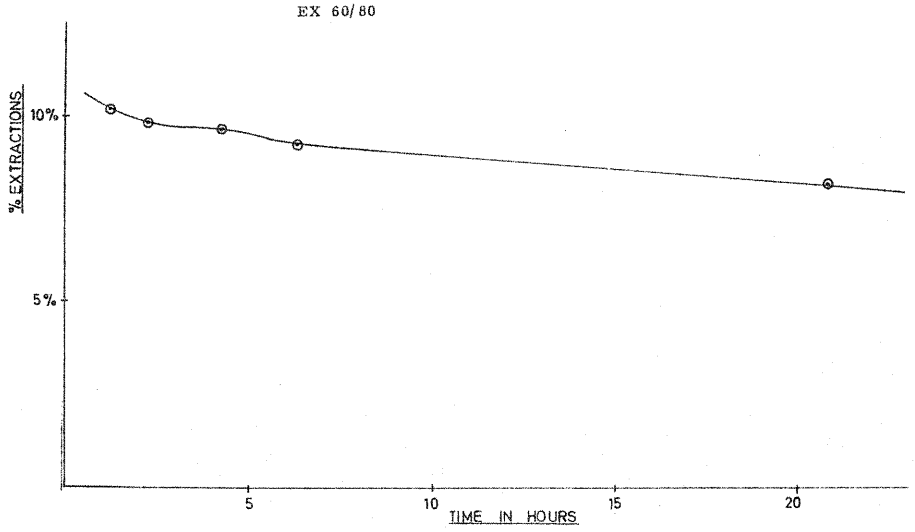

FIG. 9 ACETONE EXTRACTION % EXTRACTION V TIME
EX 60/100

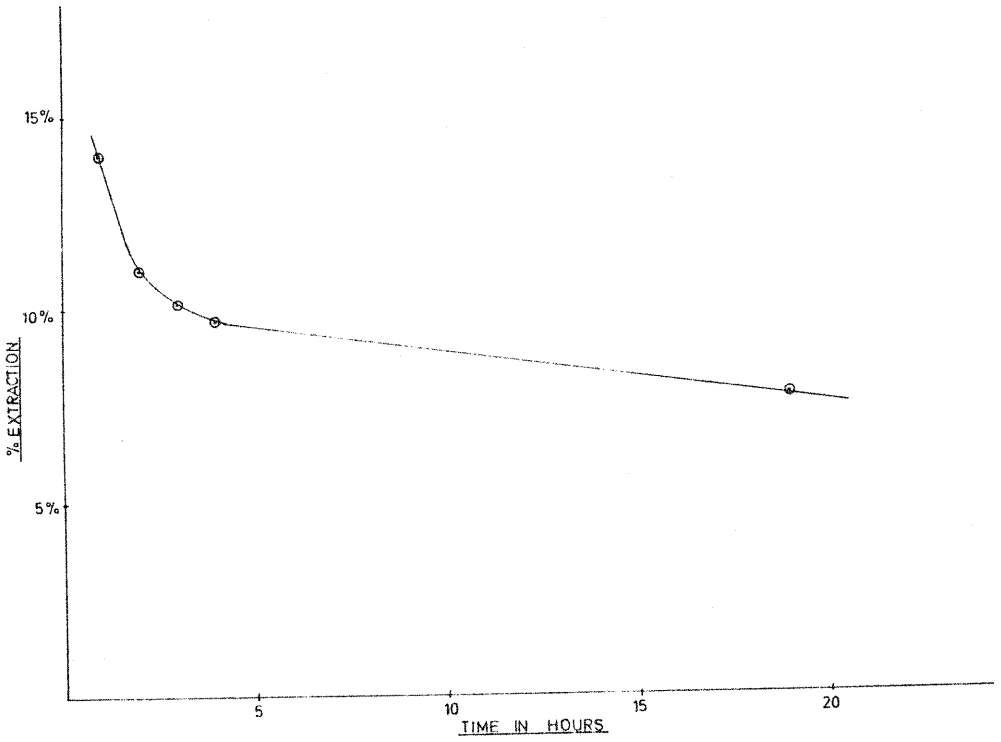

FIG. 10 ACETONE EXTRACTION % EXTRACTION V TIME
EX 118/120

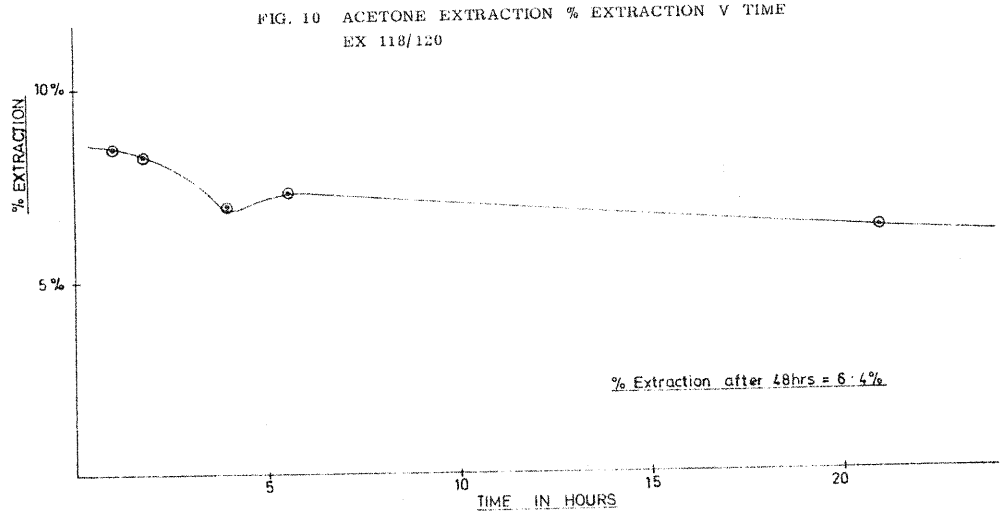

FIG. 11 ACETONE EXTRACTION % EXTRACTION V TIME
EX 118/140

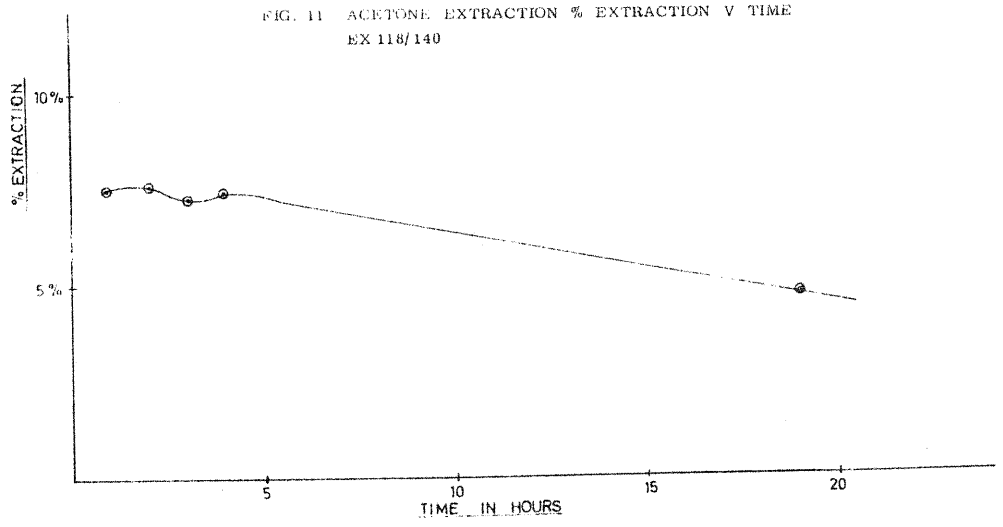

FIG. 12 ACETONE EXTRACTION % EXTRACTION V TIME
EX 118/160

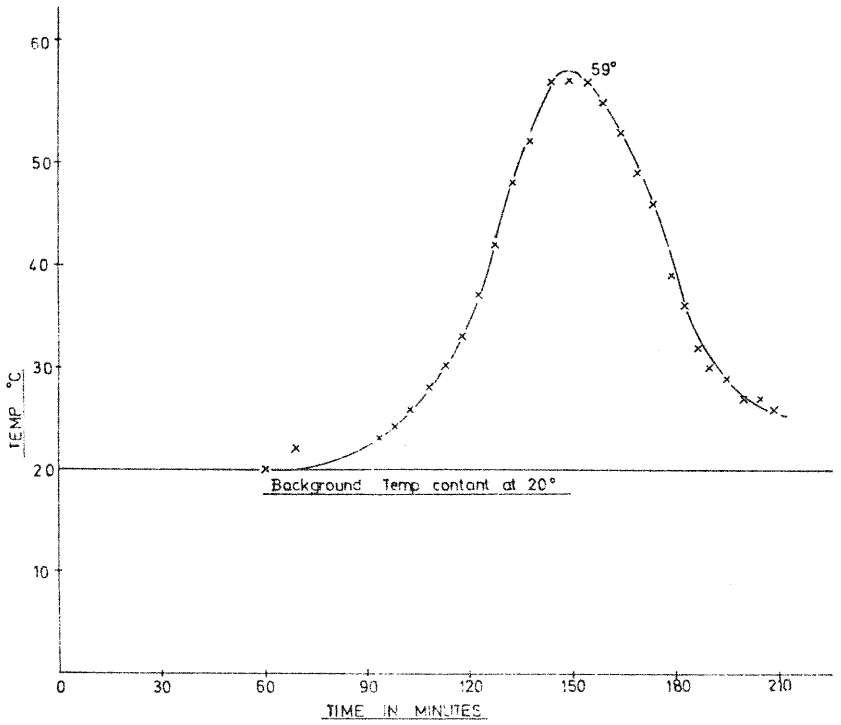

FIG. 13 POLYESTER RESINS EX 20/20

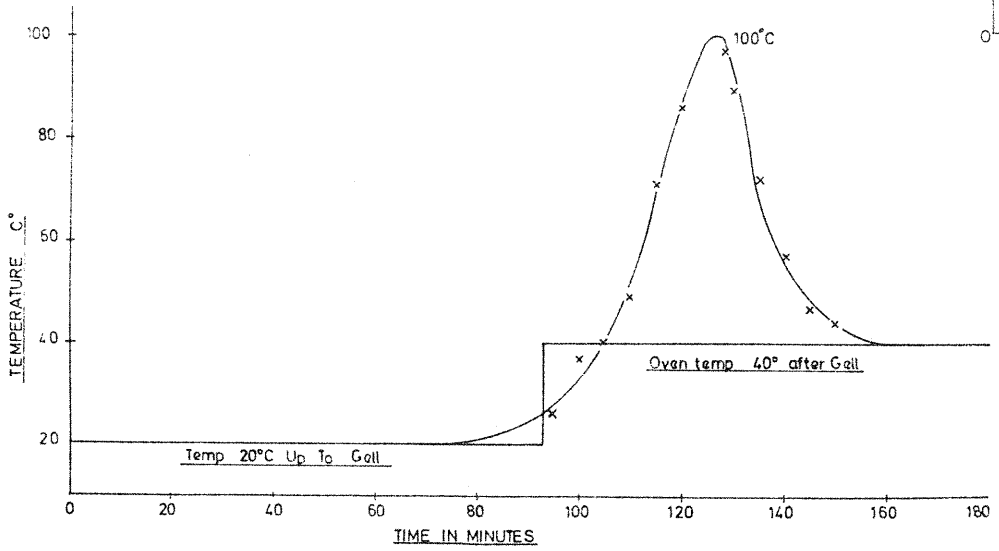

FIG. 14 POLYESTER RESINS EX 20/40

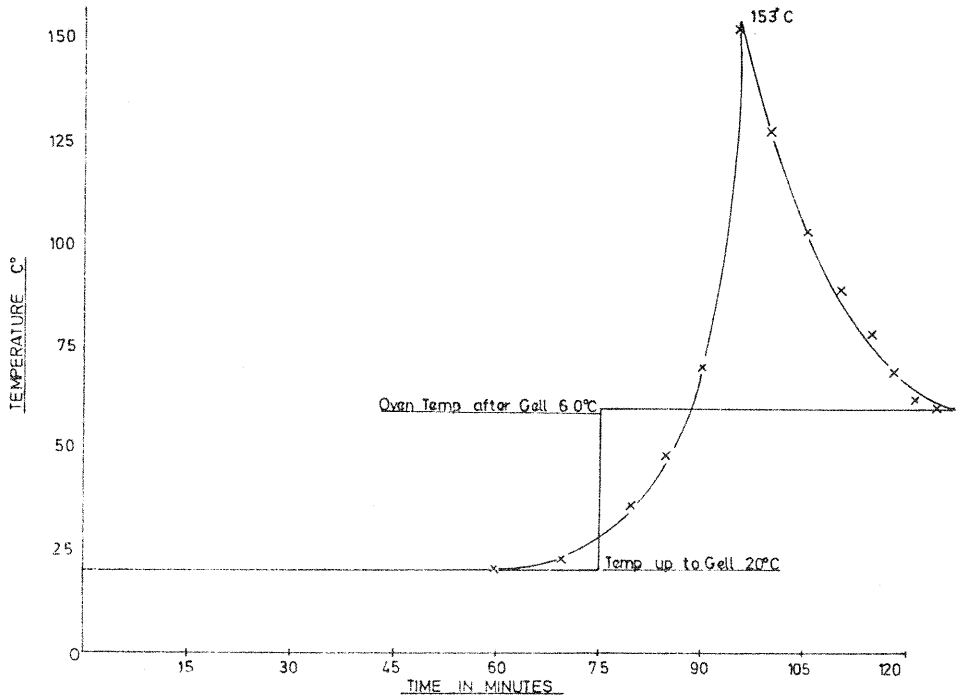

FIG. 15 POLYESTER RESINS EX 20/60

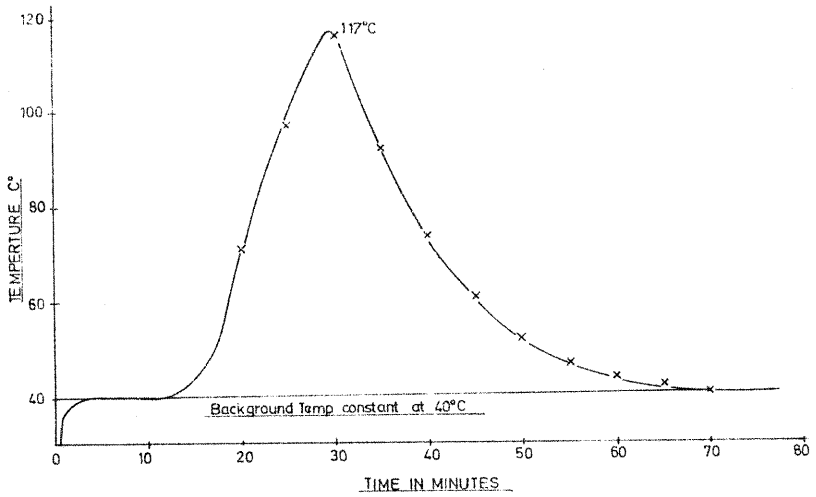

FIG. 16 POLYESTER RESINS EX 40/40

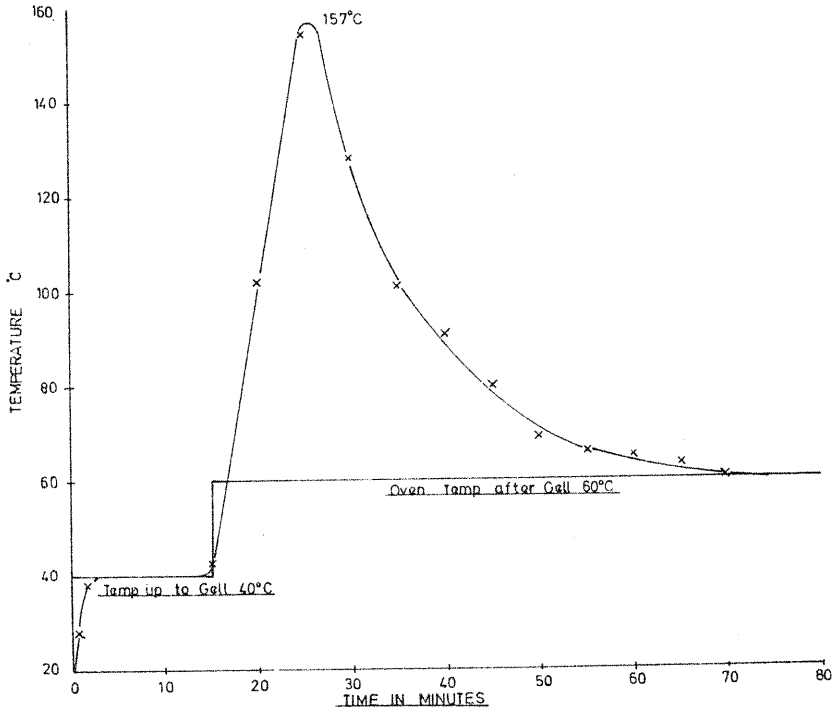

FIG. 17 POLYESTER RESINS 40/60

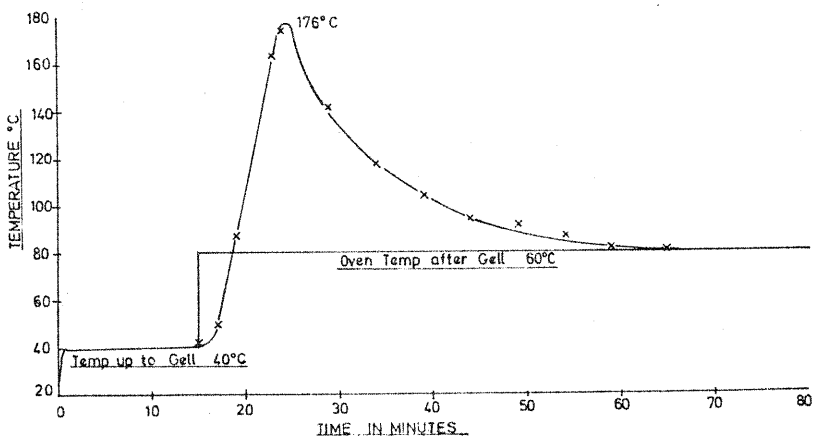

FIG. 18 POLYESTER RESINS 40/80

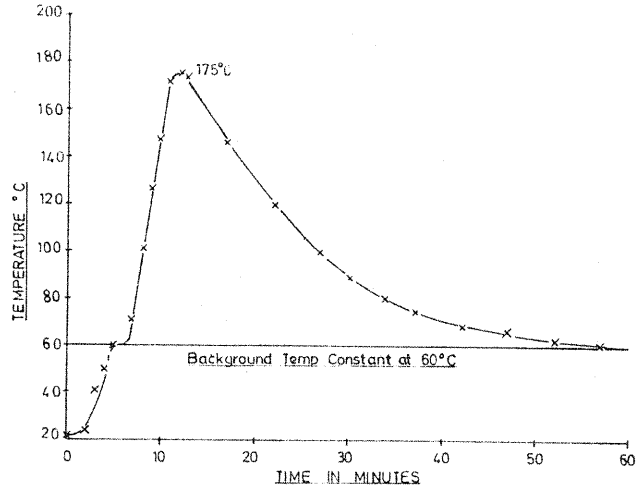

FIG. 19 POLYESTER RESINS EX 60/60

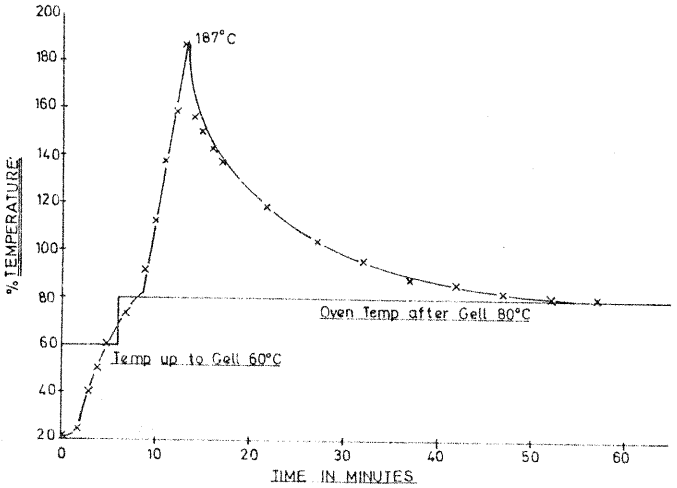

FIG. 20 POLYESTER RESINS EX 60/80

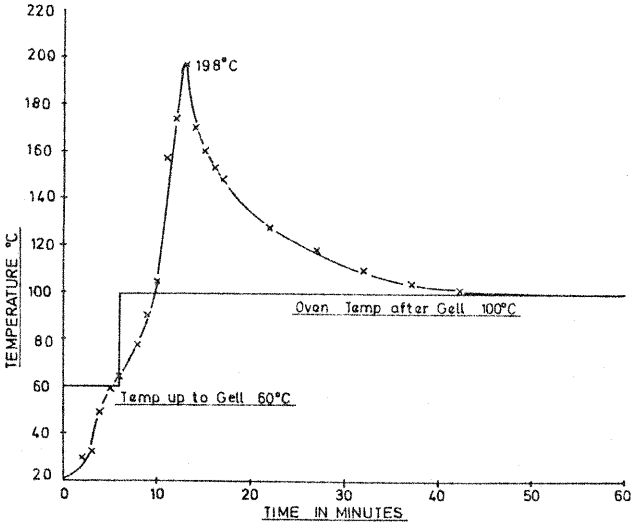

FIG. 21 POLYESTER RESINS EX 60/100