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THE "HEAT CURING OF SHELLAC".

PART I.

"LIFE UNDER HEAT"

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Shellac, and the Australian acaroids, alone amongst the natural resins possess the property of thermo-hardening. The property is in many ways similar to the 'going-over' under heat exhibited by the phenol-formaldehyde type of synthetic resin, the commercial possibilities of which have been so energetically and successfully developed. Certain practical use has been made of this property of shellac, *e.g.* in the manufacture of grinding wheels, laminated mica, etc.; but efforts to utilise the reaction in other industries, *e.g.* the manufacture of heat resistant mouldings, have met with but little success. This failure is chiefly accounted for by certain peculiarities of the 'heat-curing' of shellac. An investigation has been started, therefore, to examine these peculiarities and, if possible, modify them to meet industrial needs.

If heated to about 220°C (or at lower temperatures for longer periods) shellac solidifies into a tough, horny mass, the small quantity of water eliminated during the polymerisation producing a blistered appearance. This 'cured' material, although softened to a rubber-like mass on heating, will not melt at temperatures up to, and somewhat above, the temperature at which the initial 'curing' occurred. The work described in the present paper has been confined to an investigation into the factors governing the time taken for shellac to reach this 'cured' state.

EXPERIMENTAL.

The apparatus used was a modification of that introduced by the Westinghouse Electrical Co. It consisted of a number of flat-bottomed glass specimen tubes (6″ × 1″) immersed in a heated oil-bath, each tube containing 10 grms. of the shellac under investigation. To determine the end-point, *i.e.* when the heated shellac had "cured", the tubes were each fitted with glass rods 9″ long. These rested in the molten shellac and were given a small twist from time to time. The stage was noted at which the rod twisted back slightly, owing to the 'rubbery' setting of the lac. To facilitate observation of the twisting back, the exposed end of the rod was marked with a small black spot. By this method the time of 'life under heat' for a given shellac could be reproduced at 150°C to about 5%.

Effect of temperature on the "Life under heat" was first examined. Figures for a sample of pure Kusum shellac are given in Table I and illustrated graphically in Fig. I.

TABLE I.

Temperature.	Time taken to 'cure'.
120° C	227 minutes.
130 „	168 „
140 „	136 „
150 „	75 „
160 „	53 „
170 „	32 „
180 „	23 „
190 „	18 „
200 „	16 „
210 „	10 „
220 „	8 „
230 „	7 „
240 „	6·75 „
250 „	6·5 „

Accelerators.—The shellac samples were mixed before testing with 10% of various materials. Certain of these were found to have a marked effect in shortening the 'life under heat'. The temperature of the oil-bath was maintained at 180°±3°C. In each experiment a control sample of pure shellac was examined alongside the sample mixed with accelerator. In the following list the figures given are the ratios of the 'life under heat' of the control to that of the accelerated sample, this factor being a measure of the efficiency of the accelerator:—

Hexamethylenetetramine 9·0, Aluminium chloride 5·6, Orthophosphoric acid 4·8, Urea 4·5, Ferric sulphate 4·5, Bleaching powder 4·3, Benzidine 4·3, Hexachlorethane 4·0, Cobalt nitrate 4·0, Sodium persulphate 3·9, Phenylenediamine hydrochloride 3·7, Hydrazine sulphate 3·3, Sulphurous acid 3·0, Ammonium citrate 2·7, Sodium perborate 2·7, Amino-naphthol sulphonic acid 2·7, Ammonium persulphate 2·6, Sulphanilic acid 2·6, Calcium oxide 2·5, Calcium chloride 2·2, Ammonium phosphate 2·2, Metanilic acid 2·2, Magnesium oxide 1·9, Ammonium oxalate 1·9, Ammonium nitrate 1·9, Potassium perchlorate 1·8, Ferric chloride 1·7, Ammonium molybdate 1·7, Antimony sulphide 1·7, Succinic acid 1·7, Manganese sulphate 1·6, Tetramethyl ammonium iodide 1·6, Potassium iodate 1·6, Phenylalanine 1·6, Tannic acid 1·6, Magnesium (metal powder) 1·6, Ammonium borate 1·5, Triphenyl phosphate 1·5, Chromic acid 1·5, Aluminium sulphate 1·4, Amido-acetic acid 1·4, Potassium Nitrate 1·4, Phthalic anhydride 1·3, Para-nitroso-dimethylaniline 1·3, Asparagin 1·3, Cobalt acetate 1·3, Copper carbonate 1·3, Sodium chloride 1·3, Acetic anhydride 1·2, Manganese dioxide 1·2, Sulphur 1·2, Cupric oxide 1·2, Copper oxyacetate 1·2, Molybdic acid 1·2.

Certain of these accelerators were found to be exceptionally active. A few of these have been examined in more detail, the percentage of accelerator and temperature of testing being varied. Results are indicated in Table II and illustrated in Figs. II-VI.

TABLE II.

Degree of efficiency of acceleration at 180°, 150° and 120°C.

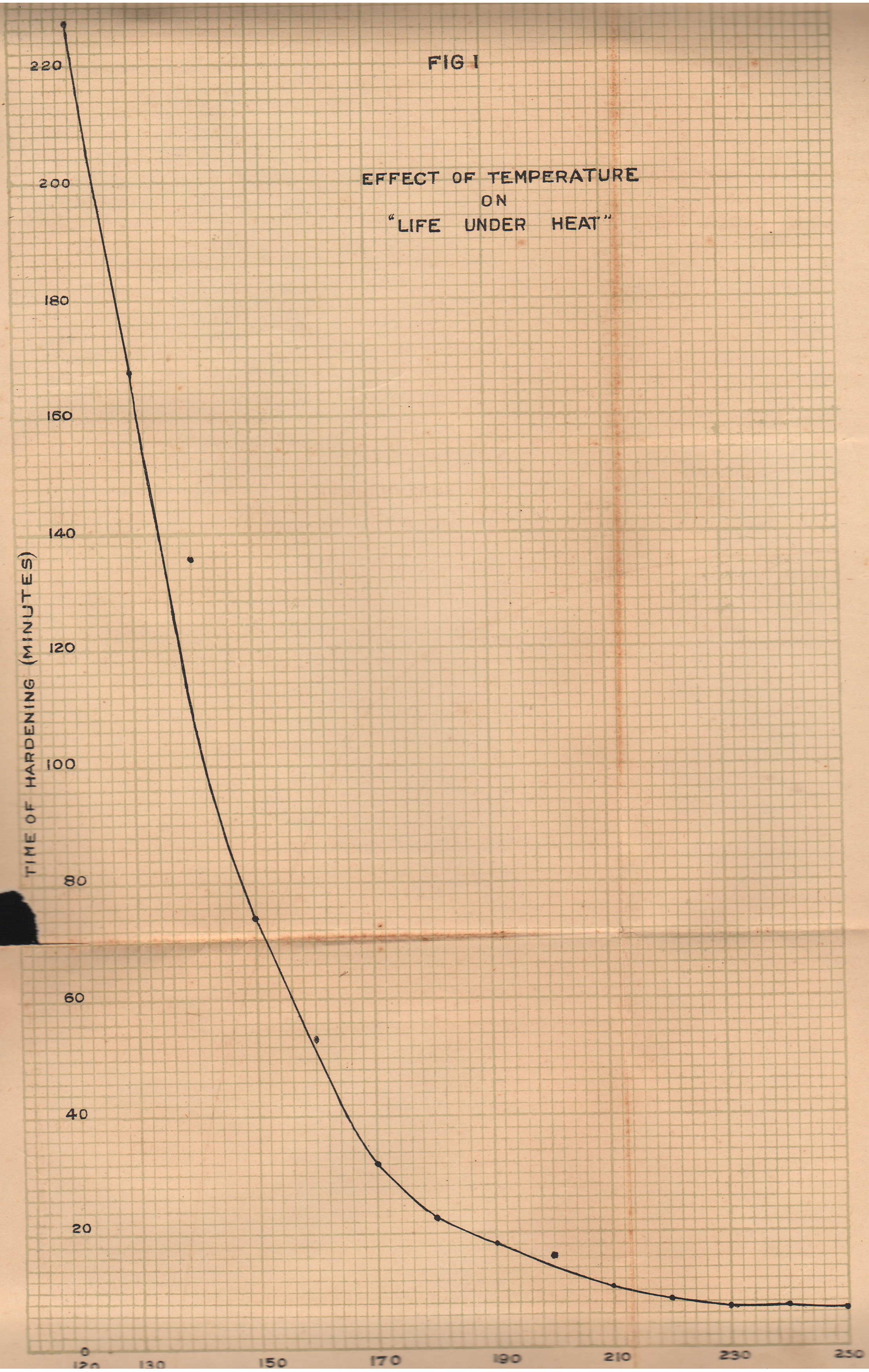
	%	180°C	150°C	120°C
Urea.	1	1·7	2·1	2·5
	2	2·2	3·6	15·0
	3	2·4	7·2	25·0
	4	2·9	8·0	30·0
	5	3·7	9·0	33·0

TABLE II.—*contd.*

	%	180°C	150°C	120°C
"Hexa".				
	1	1·1	1·3	1·3
	2	1·3	1·5	4·1
	3	1·6	3·4	7·5
	4	2·2	4·7	8·6
	5	2·6	5·4	10·0
Oxalic acid.				
	1	6·0	8·9	9·4
	2	6·0	10·0	14·3
	3	6·0	11·4	16·5
	4	7·5	11·4	19·4
	5	7·5	13·3	22·0
Citric acid.				
	1	1·9	2·3	2·0
	2	2·1	2·7	2·6
	3	2·3	3·0	3·0
	4	2·7	3·3	3·5
	5	3·0	3·6	3·9
Tartaric acid.				
	1	1·9	2·0	2·2
	2	2·2	2·8	2·4
	3	2·7	3·1	2·8
	4	3·3	3·4	3·5
	5	4·0	3·8	3·9

FIG I

EFFECT OF TEMPERATURE ON "LIFE UNDER HEAT"



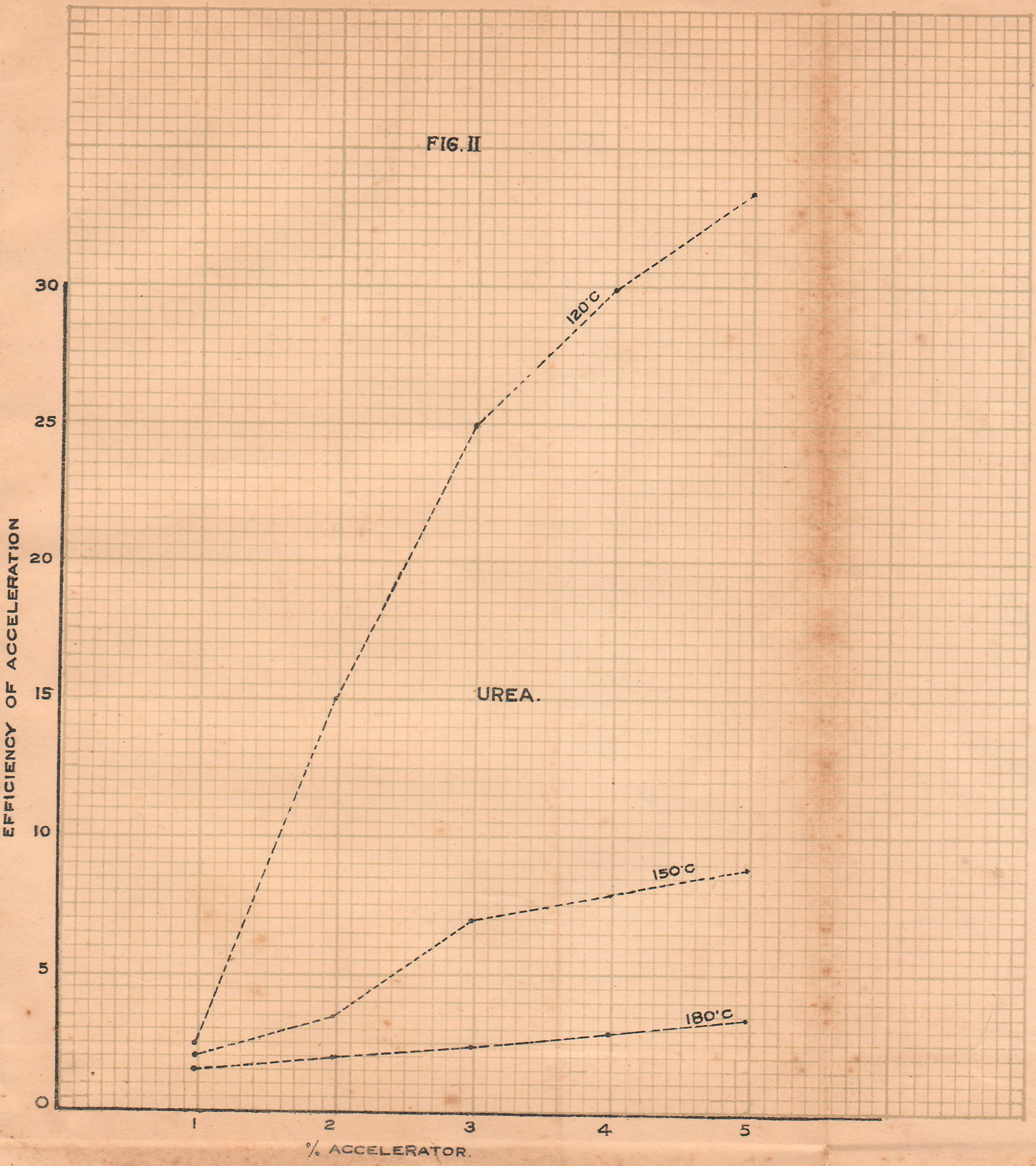


FIG. II

UREA.
120°C
150°C
180°C
EFFICIENCY OF ACCELERATION
0
5
10
15
20
25
30
% ACCELERATOR.
1
2
3
4
5

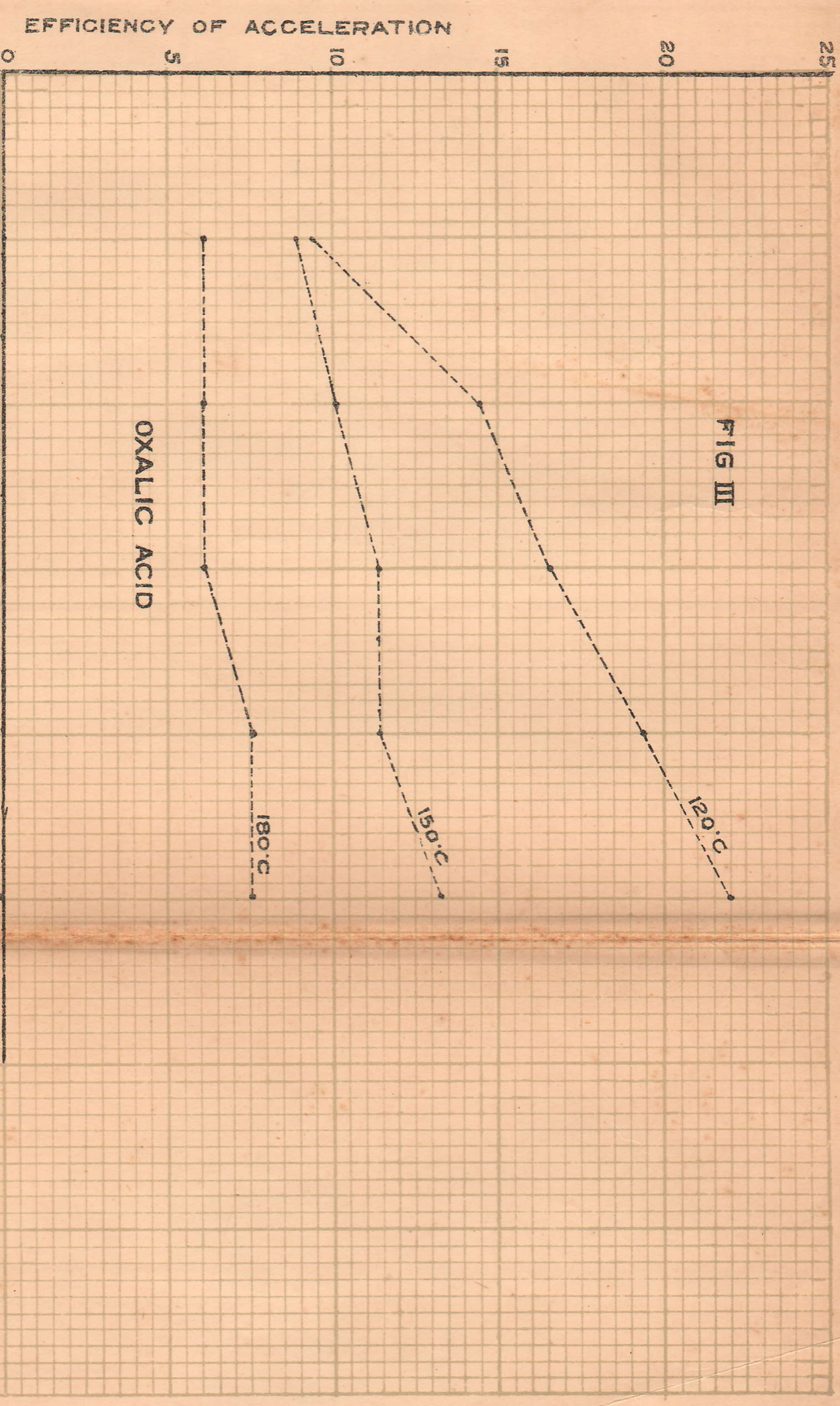


FIG III

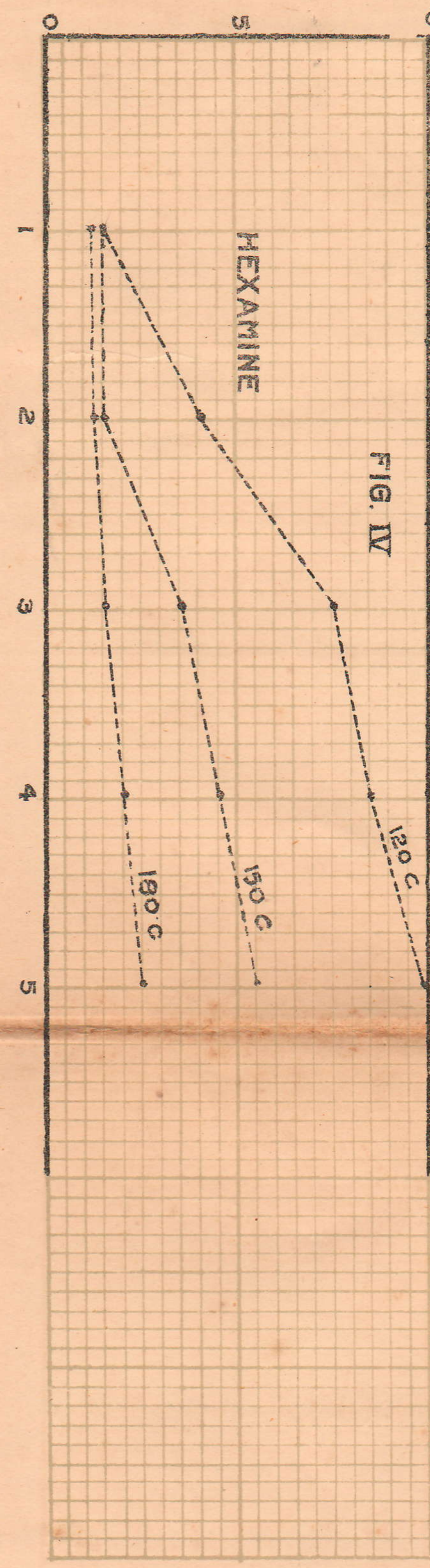


FIG. IV

FIG V

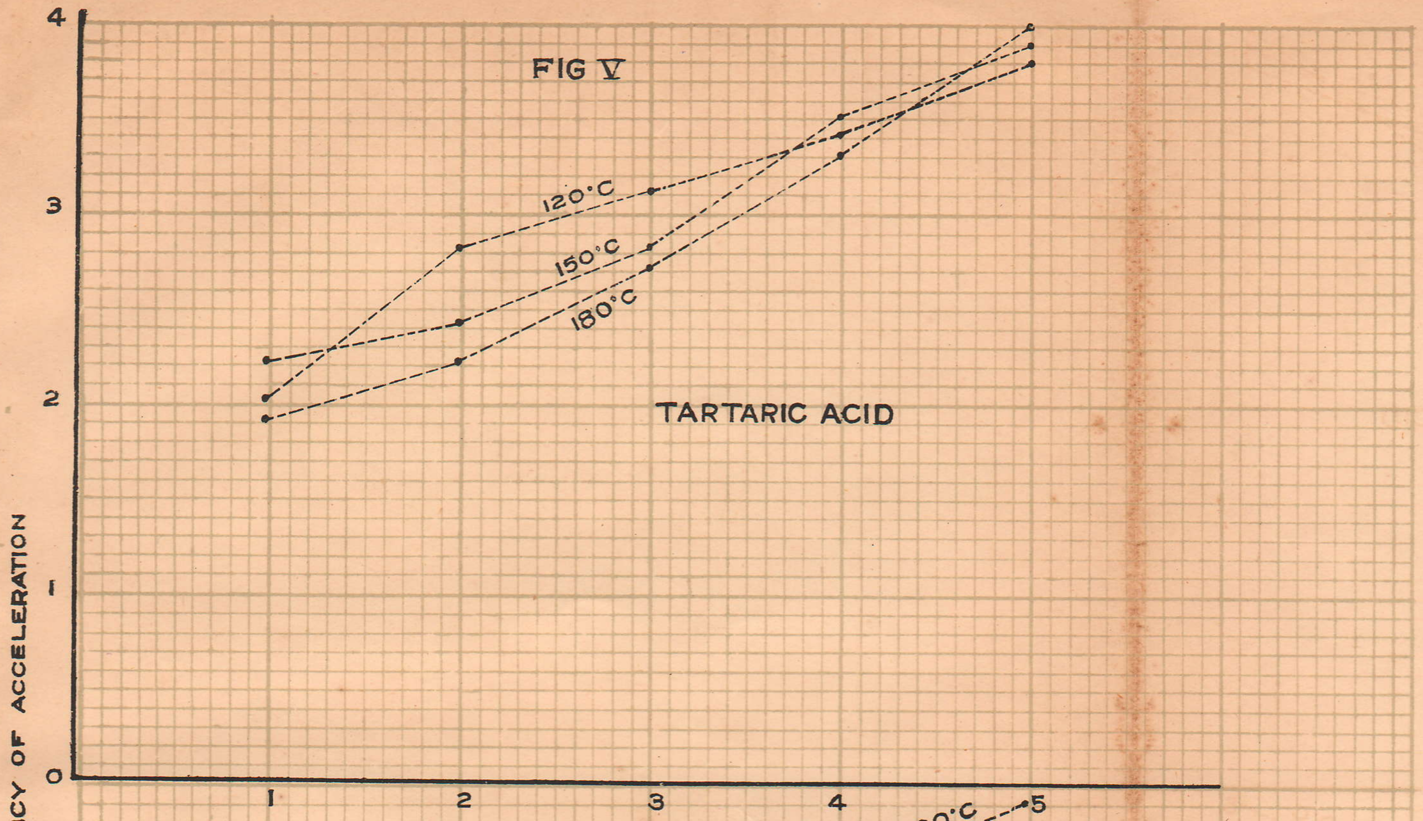
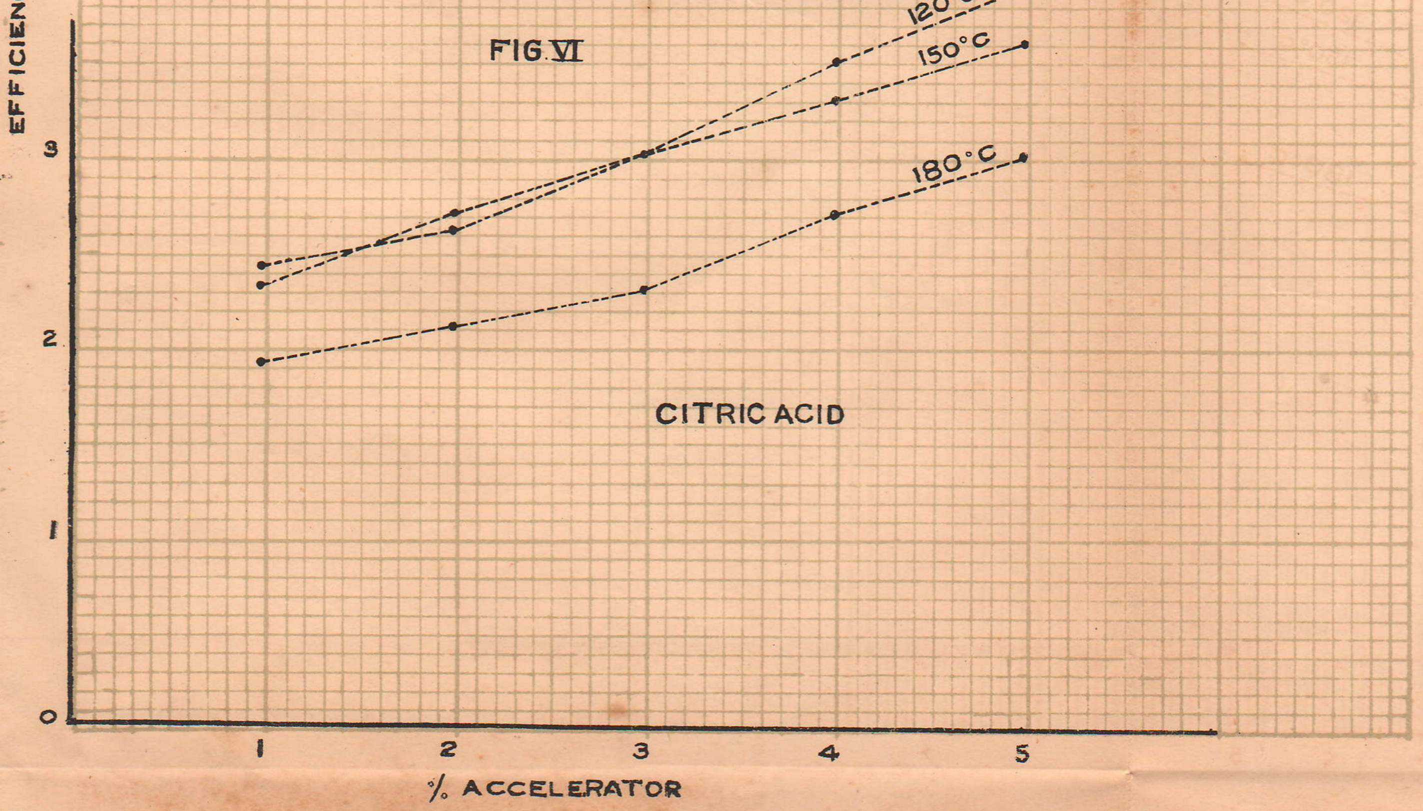

4
3
2
1
0
1
2
3
4
5
120°C
150°C
180°C
TARTARIC ACID
EFFICIENCY OF ACCELERATION

FIG VI


3
2
1
0
1
2
3
4
5
120°C
150°C
180°C
CITRIC ACID
% ACCELERATOR

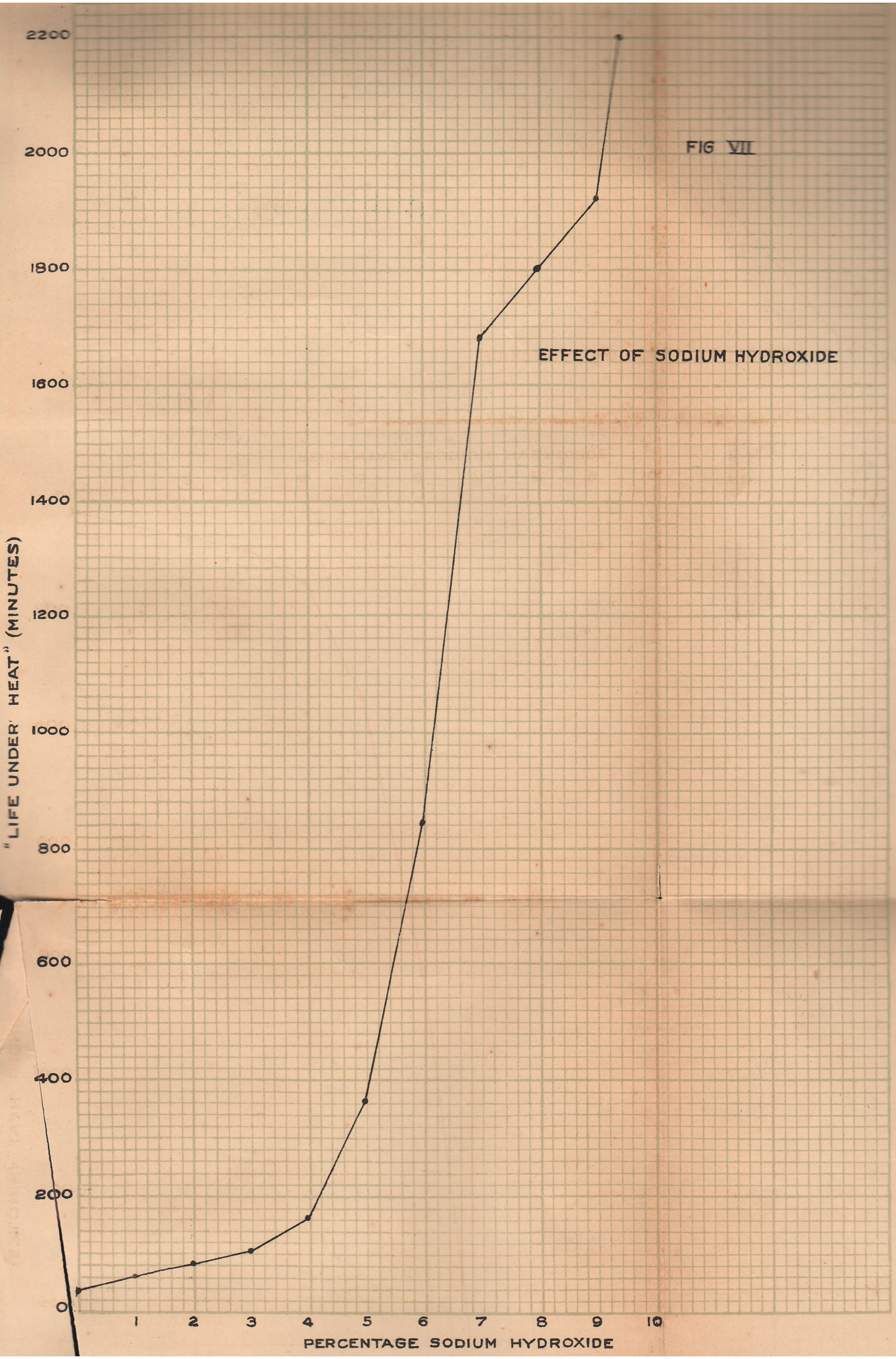


FIG VII

EFFECT OF SODIUM HYDROXIDE

TABLE II.—*contd.*

	%	180°C	150°C	120°C
Aluminium chloride.*	1	4·5	10·0	43
	2	5·4	11·7	50
	3	5·4	11·7	50
	4	5·4	11·7	50
	5	5·4	11·7	60

* Too rapid hardening to permit accurate measurement.

Sulphuric acid and hydrochloric acid are extremely powerful accelerators, even very small percentages of the dilute acids being very effective. Table III gives the results of addition of dilute (1 : 10) acid on the 'life under heat', in minutes, determined at 160°C.

TABLE III.

% dilute acid ...	0	0·5	1·0	1·5	2·0	2·5
"Life under heat" for HCl ...	44	22	19	15	10	6
,, ,, ,, H_2SO_4 ...	44	12	9	8·5	7·0	6

Escape of hydrogen chloride vapours probably detracts from the value of comparing the effects of these two acids.

Oxalic, tartaric and citric acids are also powerful accelerators as indicated in Table II.

Retarders.—A number of materials examined were found to *retard* to a varying extent the rate of curing of shellac. In each experiment a control sample was examined alongside the sample mixed with retarder. In each case 10% of retarder was added. In the following list the figures given are the ratios of the "life under heat" with and without retarder, this factor being a measure of the efficiency of the retarder :—

Sodium hydroxide 99, Potassium metal 63, Potassium hydroxide 44, Sodium carbonate 36, Sodium peroxide 33, Potassium acetate 14, Sodium acetate 11, Aniline 2·5, Tetramethyl ammonium hydroxide (10% aq. soln.) 2·1, Lead acetate 1·8, Oleic acid 1·6, Palmitic acid 1·5, Pyridine 1·5, Stearic acid 1·4, Borax 1·4, Dibutyl phthalate 1·4, Barium hydroxide 1·4, Potassium metabisulphite 1·3, Litharge 1·3, Potassium antimonate 1·3, Lactic acid 1·3. Naphthalene 1·3, Glacial acetic acid 1·3, Rosin 1·3, Dammar gum 1·3, Copal gum 1·2, Phenol 1·2.

Examination of this list indicates that the more effective of them are alkalis. The strong alkalis such as sodium and potassium hydroxides are powerful retarders. Tetramethyl ammonium hydroxide is quite a good retarder which is in agreement with the strong basic characteristics of this substance. The polymerisation of shellac in presence of alkaline materials is worthy of further investigation. As a preliminary to this study the effect of varying amounts of sodium hydroxide on 'life under heat' has been noted. Results are given in Table IV. and illustrated in Fig. VII.

TABLE IV.

% Sodium hydroxide.	Life under heat.
0	29 Mins.
1	56 ,,
2	85 ,,
3	108 ,,
4	168 ,,
5	360 ,,
6	840 ,,
7	28 hours.
8	30 ,,
9	32 ,,
10	48 ,,

Certain materials were found to have no appreciable effect on the 'life under heat'. These are indicated in the following list:—

Calcium formate, Potassium ferricyanide, Potassium ferrocyanide, Uric acid, Ferric oxide, Gum mastic, Gum arabic, Gum acacia, Gum sandarac, Gum Tragacanth, Formic acid, Guiacol, Mannitol, Sodium silicate, Potassium silicate, Sodium sulphite, Kaolin, Camphor, Piperidine & β-Naphthol.

Effect of pressure.—Samples of shellac were heated at 180°C in sealed tubes. After varying periods of time the tubes were opened and the time taken to 'cure' noted. Typical results are given in Table V.

TABLE V.

Sample.	"Life under heat".	Remarks.
Control	28·5 mins.	
Tube opened after		
30 mins	38·0 ,,	
35 ,, ...	41·0 ,,	
40 ,, ...	47·5 ,,	
43 ,, ...	51·0 ,,	
53 ,, ...	53·0 ,,	Frothed over on opening tube.
75 ,, ...	75·0 ,,	,, ,, ,,
85 ,, ...	85·0 ,,	,, ,, ,,
100 ,, ...	100·0 ,,	No frothing; the shellac had set hard.

It will be seen that pressure exerts a big retarding influence on rate of 'curing'. This is of great importance in the use of shellac as a moulding binder. In a typical experiment a sample of shellac was kept in the hydraulic press under a pressure of 1 ton per sq. in. for 210 mins. at 150°C and had not polymerised. A control sample in an open tube cures in about 75 mins. at 150°C.

DISCUSSION.

The effect of temperature on rate of 'curing' of shellac is illustrated in Fig. 1. At 220-230°C the change is very rapid, but at lower temperatures it is somewhat slow.

The retarding influence of pressure on 'curing' is important. It is an unfortunate property from the moulders' point of view, and will necessitate special moulding procedure to avoid it. This property may be useful, however, in processes dealing with molten shellac, where long 'life under heat' is desired, *e. g.*, the thermo-plastics and sealing-wax industries.

The effect of addition of reagents on the time of 'curing' has been indicated. Examination of the results suggests a rough classification of these reagents. Retarding materials include alkalis and solvents. Accelerating materials include acids, ester-forming catalysts, ammonia and substances liberating ammonia. Acids such as palmitic and oleic tend to dissolve shellac on heating and are therefore retarders.

Fig. VII illustrating the retarding effect of sodium hydroxide is interesting. The marked change in rate of 'curing' after addition of sufficient alkali to completely neutralise the free shellac acids is indicated.

In Table III certain of the more powerful accelerators are examined in greater detail. Urea is of special interest in that its accelerating efficiency increases rapidly at lower temperatures. The need for further examination of these and other accelerators is indicated and this work is in progress.

The generally accepted theory for the process of 'curing' of shellac has been summarised in a recent paper by Nagel and Baumann (2). It is believed that part of the shellac acids are present as lactones and therefore exhibit a strong tendency to aggregation (3). The water given off during hardening is assumed to be split off by condensation of two carboxyl groups of the free shellac acids present. The process consists therefore, of (*a*) an aggregation of the units of the shellac resin into massive molecular aggregates and (*b*) a small amount of anhydride formation. This theory agrees with the experimental observations of the present investigation but it would appear that insufficient importance is attached to the part played by the anhydride formation. The various accelerators are, in general, those which would be expected to accelerate the process of splitting off water. Prevention of this water formation by protecting the free carboxyl groups with sodium effects a big retarding influence. The effect of pressure in preventing ready removal of water would be expected to retard anhydride formation but not molecular aggregation. The part played by urea and ammonia-liberating substances is not so clear. It is possible that the aggregation process is accelerated by these materials. Experiments investigating this possibility are in progress.

The use of the various methods of retarding or accelerating the curing of shellac in the commercial applications of this material is indicated and certain possibilities are being examined, *e. g.* the possibility of assisting the solution of shellac in drying oils by means of 'retarders' has been demonstrated (1). Interesting results have been obtained by using 'accelerators' in the preparation of shellac mouldings.

SUMMARY.

A study has been made of the factors influencing the time of heating required to 'cure' shellac. The effect of temperature has been determined

and illustrated with a graph. The retarding effect of pressure has been established. The possibility of retarding or accelerating the process by addition of certain materials has been indicated and a rough classification suggested; *e. g.* retarding materials include alkalis and solvents, while accelerators include acids, ester-forming catalysts, ammonia and ammonia liberating agents.

REFERENCES.

(1) ALDIS, R. W. :— Bull. No. 12, Indian Lac Research Institute, Ranchi.

(2) NAGEL, W. & BAUMANN, E. :—Wiss. Veroff aus den Siemens-Konzern. Vol. II, Part 2, p. 99—113.

(3) SCHEIBER & SANDIG :— "Artificial Resins" 1931, p. 57.