

Modification of total hydrolysed lac- Part 1 - preparation of rebulac

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TOTAL hydrolysed lac has been converted by heating at 150°C to a product termed **rebulac** (for rebuilt lac) having diversified uses similar to lac but with improved properties. It is a tough, dark and slightly mass having a cold flow; soluble in all usual shellac solvents and unlike shellac in ethers and esters. The most notable deviation is its low hydroxyl value of 87 as against 250 of shellac. Like shellac, it is also a mixture of several components probably of different molecular dimensions. The carboxyl, hydroxyl and aldehydic groups of the free constituent acids of total hydrolysed lac had combined predominantly through ester and acetal linkages to form rebulac. Further more, the polyesterification reaction appeared to follow a third order; while the polyacetal formation a second order.

In an earlier communication an easy and economic method for the preparation of total hydrolysed lac from refuse lacs or seedlacs and its properties were reported. In this paper a method for its modification by the application of heat only is being presented.

The hydrolysed lac is a dark, soft and sticky mass and comprises all the constituent acids of lac resin in free state. It is expected to be an interesting raw material for modification to suitable end products having diversified uses similar to lac itself but with improved properties.

EXPERIMENTAL

Total hydrolysed lac prepared by passing alcoholic lac hydrolysate through cation exchange resin was taken for study.

A number of experiments on the heat polymerisation of hydrolysed lac were carried out at 150°, 175° and 200°C and the following procedure has been adopted to arrive at the desirable end product having suitable properties and film performances.

Hydrolysed lac is heated at 150°C with constant stirring in a porcelain or stainless steel vessel. The capacity of the vessel should be at least 3 times the volume of hydrolysed lac taken in order to allow sufficient space for spontaneous frothing during the first 2 hr of heating. Heating and stirring are con-

tinued till the total heating period is short by 30 to 40 min of the actual polymerisation time. The thick hot melt is then poured out on a flat surface where the product cools down to a tough, dark and slightly tacky mass. The products thus obtained have been termed as "Rebulac" which stands for rebuilt lac obtained by heat polymerisation only.

RESULTS AND DISCUSSION

The effect of various catalysts on the heat polymerisation of total hydrolysed lac at 150°C has been reported. The products obtained by polymerisation with oxalic acid and maleic anhydride were brittle and highly dark, with p-toluene sulphonic acid spongy and highly dark while with phosphoric acid elastic and light coloured. The one without any catalyst was also elastic, tough and dark coloured. Toughness, elasticity and their power to stick to metallic surfaces suggested their possible application in the fields of surface coating and adhesives. Since the above products were not completely soluble in common organic solvents, end products for examination were prepared by continuing the polymerisation in presence or absence of catalyst upto the pregelation stage. Preliminary studies on the film properties of these products were carried out. In general the films were tacky and could only be made tack free after prolonged baking at 150°C except for the product without any catalyst. The backed films were, of course, smooth and glossy. The results are brought out in Table-I. It will be noted from the table that the product obtained without any catalyst showed encouraging film performances almost in every respect indicative of further thorough investigation.

Life of hydrolysed lac at 150°, 175° and 200°C was determined at the outset and sufficient amounts were heated in stainless steel beakers at the above temperatures for a period short by 10-20 min. of their polymerisation time. The product obtained at 150°C was hard but tacky and adhered firmly to the container, the one at 175°C less tacky and the one at 200°C hard and brittle. The products were soluble in lower alcohols, esters, ketones, ethers, and aqueous inorganic and organic basis, partially in

TABLE I — FILM PROPERTIES OF HYDROLYSED LAC MODIFIED WITH THE CURING AGENTS, IN SPIRIT VARNISHES (25 PERCENT)

No. Sl.	Properties	Control (Hydrolysed lac)	Hydrolysed lac modified by heating at 150°C with 5 percent of		
			Urea for 20 hr	Maleic anhydride for 6 hr	Phosphoric acid for 3.5 hr
1.	Appearance	Smooth, uniform and tacky	Smooth, uniform and tacky	Smooth, uniform and tacky	Smooth, uniform, glossy but tacky
2.	Baking time at 150°C to make the film tack-free (hr)	4	2.4	4	2
3.	Scratch hardness on 1 mm steel ball (gm)	600	600	600	700
4.	Water resistance (time for initial blush) (hr)	2.75	2.50	2.75	3.00
5.	Flexibility (panel bend round 3 mm mandrel)	No crack	No crack	No crack	No crack

TABLE 2 — PROPERTIES OF PRODUCTS OBTAINED BY POLYMERISING HYDROLYSED LAC DIFFERENT TEMPERATURES

Products	Chemical Properties				Properties of film pigmented with titanium dioxide and baked at 150°C for 30 min.			
	Appearance	Acid value	Saponification value	Hydroxyl value	Gloss (Lange's Glossometer)	Flexibility (panel bent round 3mm mandrel)	Water resistance (7 days immersion)	Scratch hardness on 1 mm steel ball (gm)
I	Dark, hard and slightly tacky	82	212	87	69	No crack	Slight blush	1700
II	Dark, hard and very slightly tacky	105	212	132	31	No crack	No effect	2000
III	Dark, hard and brittle	135	210	148	22	Crack	No effect	2000

I = Product obtained by heating total hydrolysed lac at 150°C for 330 min.
 II = Product obtained by heating total hydrolysed lac at 175°C for 135 min.
 III = Product obtained by heating total hydrolysed at 200°C for 45 min.

chloroform and benzene but insoluble in pet-ether, toluene and white spirit. Chemical constants of the products and their film properties from aqueous medium are shown in Table-2.

It will be evident from the table that there are hardly any appreciable difference except gloss in the film properties of the three products. Since the life at higher temperature are shorter and chances of controlling the reaction towards desirable end products remote, attention was focussed on the product obtained by heating at 150°C.

PROPERTIES OF REBULAC PREPARED AT 150°C

The Rebulac prepared by adopting the procedure given under experimental appeared to have very interesting properties. It is similar to shellac in many aspects and different in a few. It is a tough, dark and slightly tacky mass having a cold flow and soluble in all usual shellac solvents and again like shellac in aqueous alkalies also. The most characteristic different in contrast to shellac is its complete solubility in ethers and esters. The chemical and

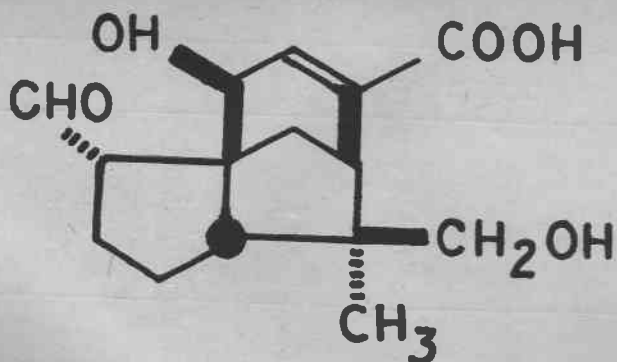
TABLE 3 — COMPARATIVE CHEMICAL AND PHYSICAL PROPERTIES OF HYDROLYSED LAC, REBULAC AND SHELLAC

Sl. No.	Properties	Total Hydro-lysed lac	Rebulac	Shellac
1.	Acid value	206	80-82	79-80
2.	Saponification value	212	212	210
3.	Hydroxyl value	360	87	250
4.	Carboxyl value	60	14	18
5.	Iodine value	22-24	16	16
6.	Vicinal hydroxyl group (% in terms of aleuritic acid)	35-36	17-18	14-15
7.	Molecular weight (Rest)	264 (Fqu. wt)	1100	980
8.	Melting point (°C)	Soft mass	55-60	75-80
9.	Life under heat at 750°C (min)	380	36	57
10.	Flow (Victor method) (mm)	—	134	64
11.	Colour Index	—	23	13

physical properties are brought out in Table-3. For the sake of comparison the corresponding properties of the original hydrolysed lac and shellac prepared from the same source are also included.

Lac hydrolysate contains mainly aliphatic and terpenic acids of which the major being aleuritic (I) and jalaric (II) constituting ~ 60 percent of total.

Structures enclosed



These two are tetrafunctional while the rest are di-, tri- and also tetra-functional; the reactive groups —COOH, being and —OH. The possible reactions which are likely to occur during the heat polymerisation are as follows :-

(i) Reaction between the carboxyl and hydroxyl groups (ester formation), (ii) Reaction between hydroxyl and carbonyl groups (acetal formation); (iii) Reaction between carboxyl and carbonyl groups (acylal formation); (iv) Reaction between two hydroxyl groups (ether formation) and (v) Reaction between hydroxyl group and adjacent hydrogen atom (unsaturation formation).

It will be evident from the data in Table-3, that lower values such as acid, hydroxyl, carbonyl, vicinal hydroxyl, are indicative of reaction among the

—COOH, —CHO and —OH groups, suggesting the possibility of all the first four types of reactions being involved. The decrease in iodine value rules out reaction (v) and though it is not very clearly understood, there may be some sort of combination through the unsaturated linkage.

The most notable deviation of rebulac is its low hydroxyl value of 87.0 as against that of 250.0 for shellac. Its carbonyl value (14.0) underwent no change on hydrolysis which is also in great contrast to shellac where the value increases. This further

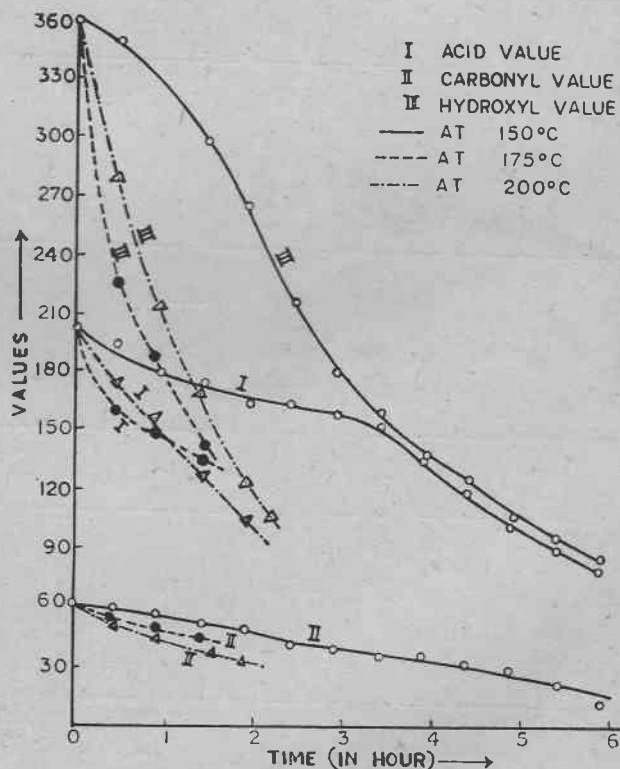


FIG. 1:- PROGRESSIVE FALL OF ACID(I) CARBONYL(II) AND HYDROXYL (III) VALUES OF TOTAL HYDROLYSED LAC WITH TIME AND TEMPERATURE.

indicates that there is no acylal formation ruling out reaction (iii) but formation of acetal linkages only by reaction (ii). Though there is no concrete evidence for the formation of any ether linkages by reaction (iv), it cannot be ruled out that this type of reaction has not occurred. The simultaneous fall in

acid and hydroxyl values indicate the formation of ester linkages by reaction (i). As is expected, there was no appreciable change in the saponification value indicating further that under the conditions there were no decarboxylation but only esterification. Hence considering all the facts, it can be safely said

TABLE 4 — EFFECT OF HEAT ON HYDROLYSED LAC AT 150°C

Sl. No.	Heating time (hr)	Acid value	% decrease in acid value	Hydroxyl value	% decrease in hydroxyl value	Carbonyl value	% decrease in carbonyl value	Saponification value	% of vicinal OH in terms of aleuritic acid	% decrease in vicinal OH group
1.	0.0	206.0	0.00	360.0	0.00	60.3	0.00	212.5	35.0	—
2.	0.5	191.0	7.28	348.0	3.33	57.3	4.98	212.7	—	—
3.	1.0	180.0	12.62	329.0	8.61	54.2	10.11	212.5	—	—
4.	1.5	173.0	16.02	297.0	17.50	51.0	15.42	211.9	—	—
5.	2.0	165.0	19.90	263.0	26.94	47.5	21.23	210.8	—	—
6.	2.5	163.0	20.87	215.0	40.28	44.8	25.70	211.7	—	—
7.	3.0	158.0	23.30	179.0	50.28	39.9	33.83	212.1	—	—
8.	3.5	152.0	26.21	159.0	55.83	38.3	36.48	212.16	—	—
9.	4.0	134.0	34.95	136.0	62.22	34.5	42.79	212.4	—	—
10.	4.5	121.0	41.26	124.0	65.55	31.5	47.76	212.5	—	—
11.	5.0	105.0	49.03	105.0	70.83	27.6	54.23	211.8	—	—
12.	5.5	93.0	54.85	93.0	74.16	21.8	63.85	212.4	—	—
13.	6.0	82.0	60.20	87.0	75.83	11.3	81.26	212.1	17.0	51.43
14.	6.2									

Polymerized

TABLE 5 — EFFECT OF HEAT ON HYDROLYSED LAC AT 175°C

Sl. No.	Heating time (hr)	Acid value	% decrease in acid value	Hydroxyl value	% decrease in hydroxyl value	Carbonyl value	% decrease in carbonyl value	Saponification value	% of vicinal OH in terms of aleuritic acid	% decrease in vicinal OH group
1.	0.0	206.0	0.00	360.0	0.00	60.3	0.00	212.5	35.0	—
2.	0.5	173.0	16.02	280.0	22.22	51.8	14.10	210.3	—	—
3.	1.0	158.0	23.30	215.0	40.28	44.5	26.20	209.8	—	—
4.	1.5	124.0	39.80	167.0	53.62	38.7	35.82	212.3	—	—
5.	2.0	103.0	50.00	121.0	66.39	35.0	41.96	211.3	19.0	45.71
6.	2.5									

Polymerized

TABLE 6 — EFFECT OF HEAT ON HYDROLYSED LAC AT 200°C

Sl. No.	Heating time (hr)	Acid value	% decrease in acid value	Hydroxyl value	% decrease in hydroxyl value	Carbonyl value	% decrease in carbonyl value	Saponification value	% of vicinal OH in terms of aleuritic acid	% decrease in vicinal OH group
1.	0.0	206.0	0.00	360.0	0.00	60.3	0.00	212.5	35.0	—
2.	0.5	167.0	18.93	235.0	34.72	56.2	6.80	211.3	—	—
3.	1.0	149.0	27.67	187.0	48.05	48.6	19.40	209.5	—	—
4.	1.5	135.0	34.45	141.0	60.82	44.0	27.04	210.8	19.5	44.28
5.	1.7									

Polymerized

that the first two types of reactions are predominantly responsible for the formation of rebulac from total hydrolysed lac.

Due to the condensation reactions there is increase in molecular weight but no indication of any higher polymer. However, like shellac it is also a mixture of several components²³ which may be of different molecular dimensions. Thin layer chromatographic study (solvent system :- trichloroethylene: chloroform: methanol — 9:10:2, v/v) revealed that it is composed of at least six components.

Rebulac has been found to cure melamine resin in the cold just in the same manner as shellac⁴ and films of improved properties are obtained. It also reacts readily with tolylene di-isocyanate in acetone or methyl ethyl ketone medium. The gelation time with 20 per cent di-isocyanate is nearly 4 hrs. and the films are hard, glossy and resistant to water for more than 30 days. This behaviour of rebulac with di-isocyanate is also in great contrast to shellac which gels readily under the same condition with the addition of only 6 per cent of di-isocyanate⁵⁶.

KINETICS OF POLYMERISATION

It has been mentioned earlier that most of the chemical constants of hydrolysed lac decrease on condensation polymerisation due to combination of the free constituent acids mainly through their carboxyl, hydroxyl and aldehyde groups. In order to find out the effect of heating with time on the progress of polymerisation of hydrolysed lac at 150°, 175° and 200°C, samples were drawn at timed intervals and their constants determined. The data obtained are presented in Tables 4 to 6 and graphically in Fig. 1.

Examination of the tables reveals several significant points First, the saponification value remained constant all through out, confirming our earlier view

TABLE 7 — CALCULATION OF \bar{p} , $1/1-\bar{p}$, $(1/1-\bar{p})^2$, K_1 and K_2 AT 150°C FOR POLYESTERIFICATION REACTION

Sl. No.	Heating time (hr)	A. V.	p.	1		$K_1 \times 10^2$	$K_2 \times 10^6$
				$1-\bar{p}$	$(1-\bar{p})^2$		
1.	0.5	191.0	0.0728	1.079	1.164	0.7669	3.865
2.	1.0	180.0	0.1262	1.144	1.311	0.7039	3.664
3.	1.5	173.0	0.1602	1.191	1.418	0.6189	3.283
4.	2.0	165.0	0.1990	1.248	1.559	0.6019	3.287
5.	2.5	163.0	0.2087	1.264	1.598	0.5126	2.818
6.	3.0	158.0	0.2330	1.304	1.700	0.4919	2.749
7.	3.5	152.0	0.2621	1.355	1.837	0.4923	2.814
8.	4.0	134.0	0.3495	1.538	2.363	0.6529	4.012
9.	4.5	121.0	0.4126	1.702	2.892	0.7573	4.967
10.	5.0	105.0	0.4903	1.962	3.850	0.9339	6.714
11.	5.5	93.0	0.5485	2.215	4.905	1.0724	6.225
12.	6.0	82.0	0.6019	2.512	6.313	1.2233	6.147
13.	6.2			Polymerized			

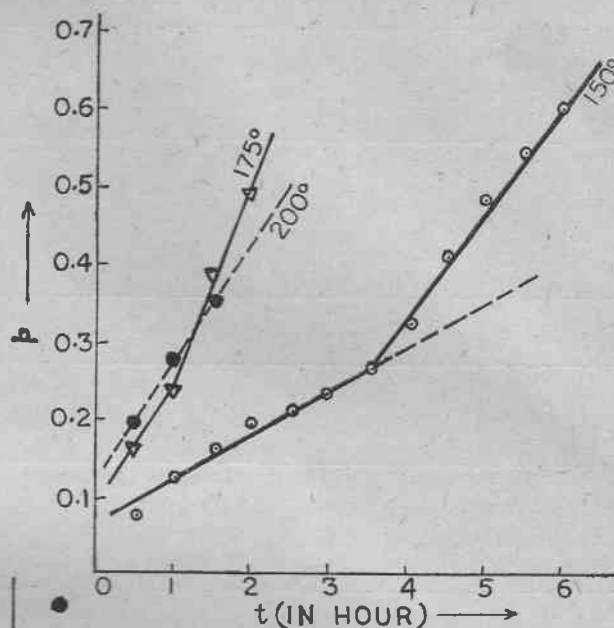


FIG. 2.—t, p CURVE FOR POLYESTERIFICATION

that there is no combination of the carboxyl group other than simple esterification only. Second, there is gradual decrease in the values of acid, hydroxyl and carbonyl. Third, the percent decrease in the values are more pronounced at 150°C, obviously due to the longer reaction time at this temperature. In fact, just prior to the gel point more than 60 percent of carboxyl, 75 percent of hydroxyl and 80 percent of carbonyl groups have been consumed. Fourth, as expected due to polyfunctionality of the reacting constituents there were gel formation very easily at temperatures higher than 150°C. Fifth, two types of reactions occur, e.g. polyesterification and polyacetal formation. Sixth, the secondary (vicinal) hydroxyls are more reactive i.e. their participation are predominant as their percent decrease is more than 65 of the total hydroxyl consumed.

TABLE 8 — CALCULATION OF p , $1/1-p$, $(1/1-p)^2$, K_2 and K_3 AT 175°C FOR POLYESTERIFICATION REACTION

Sl. No.	Heating time (hr)	A. V.	p	$\frac{1}{1-p}$	$\frac{1}{(1-p)^2}$	$K_2 \times 10^3$	$K_3 \times 10^3$
				$1-p$	$(1-p)^2$		
1.	0.5	173.0	0.1602	1.191	1.418	1.854	0.9803
2.	1.0	158.0	0.2331	1.304	1.700	1.476	0.8248
3.	1.5	124.0	0.3981	1.661	2.759	2.189	1.3810
4.	2.0	103.0	0.5000	2.000	4.000	2.427	1.7670
5.	2.5			Polymerized			

TABLE 9 — CALCULATION OF p , $1/1-p$, $(1/1-p)^2$, K_2 and K_3 AT 200°C FOR POLYESTERIFICATION REACTION

Sl. No.	Heating time (hr)	A. V.	p	$\frac{1}{1-p}$	$\frac{1}{(1-p)^2}$	$K_2 \times 10^3$	$K_3 \times 10^3$
				$1-p$	$(1-p)^2$		
1.	0.5	167.0	0.1893	1.233	1.522	2.262	1.230
2.	1.0	149.0	0.2767	1.382	1.912	1.854	1.070
3.	1.5	135.0	0.3446	1.526	2.328	1.702	1.040
4.	1.7			Polymerized			

Examination of the graph further reveals that at 150°C the hydroxyl value decreased rapidly showing a steep fall from 362 to 160 within the first 3.5 hr. followed by a gradual fall thereafter while the acid value decreased progressively from 206 to 150 during the first 3.5 hr. and then rapidly. On the other hand, the carbonyl value maintained a progressive fall all through. At 175° and 200°C, however, the hydroxyl

and acid values showed steep fall only while the carbonyl a progressive fall.

As has been envisaged that the two main types of reaction taking place simultaneously during the condensation are polyesterification and polyacetal formation. To verify this, the time for reaching 20 percent conversion has been noted at the three temperatures and from the arrhenius plot the energy of activation, E , calculated. The values 11.18 and 22.14 Kcal/mol, though nearer to 15.0 and 30.0 respectively which are characteristic of esterification and acetal formation, cannot be confirmed with certitude. Most probably the values have been lowered due to the simultaneous reactions.

The degree of polymerisation p , and $1/1-p$ and $(1/1-p)^2$ were calculated (Tables 7 to 9) and their plots against t (Figs. 2 to 4) drawn for the polyesterification reaction at the three temperatures. These plots also do not give any correct picture which can exclusively corroborate only one type of reaction. It will be evident from the Figs. that especially at 150°C there are in every case two straight lines having different slopes at 3.5 hr. stage. It might be contended that it is at this stage the change in the nature of reaction takes place. It is also difficult to say from the plots that any of these represent truly one kind of reaction or an overall type. On close examination we find too that none of the plots pass through the origin of the coordinates or nearer which is one of the essentials to satisfy the conditions of the equation.

In a similar way, if the plots of, p , $1/1-p$ and $(1/1-p)^2$ (Tables 10-12) against t are drawn in the case of polyacetal reaction, almost same nature of plots are obtained. In these cases the slopes of the lines are noticed to occur at 4.5 hr. stage. Therefore,

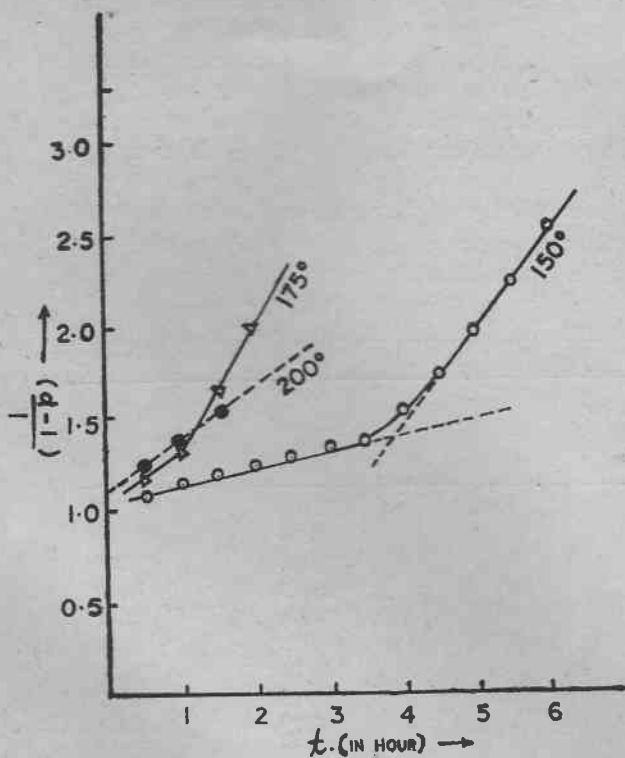


FIG. 3 : $t, \frac{1}{1-p}$ CURVE FOR POLY-ESTERIFICATION

TABLE 10 — CALCULATION OF p , $1/1-p$, $1/(1-p)^2$, K_2 and K_3 AT 150°C FOR POLYACETAL-FORMATION

Sl. No.	Heating time (hr)	C. V.	p	$1/1-p$	$1/(1-p)^2$	$K_2 \times 10^5$	$K_3 \times 10^5$
1.	0.5	57.3	0.0498	1.052	1.107	1.725	2.943
2.	1.0	54.2	0.1011	1.112	1.237	1.850	3.259
3.	1.5	51.0	0.1542	1.182	1.397	2.012	3.639
4.	2.0	47.5	0.2123	1.270	1.613	2.239	4.215
5.	2.5	44.8	0.2570	1.346	1.768	2.295	4.334
6.	3.0	39.9	0.3383	1.511	2.283	2.825	5.881
7.	9.5	38.3	0.3648	1.574	2.477	2.719	5.802
8.	4.0	34.5	0.4279	1.748	3.056	3.101	7.068
9.	4.5	31.5	0.4776	1.914	3.663	3.368	8.137
10.	5.0	27.6	0.5423	2.185	4.774	3.930	10.380
11.	5.5	21.8	0.6385	2.766	7.651	5.325	16.630
12.	6.0	11.3	0.8126	5.336	28.450	11.980	62.960
13.	6.2			Polymerized			

TABLE 11 — CALCULATION OF p , $1/1-p$, $1/(1-p)^2$, K_2 and K_3 AT 175°C FOR POLYACETAL-FORMATION

Sl. No.	Heating time (hr)	C. V.	p	$1/1-p$	$1/(1-p)^2$	$K_2 \times 10^5$	$K_3 \times 10^5$
1.	0.5	51.8	0.1410	1.164	1.355	5.439	9.763
2.	1.0	44.5	0.2620	1.355	1.836	5.887	11.49
3.	1.5	38.7	0.3582	1.558	2.427	6.169	13.08
4.	2.0	35.0	0.4196	1.723	2.969	5.995	13.54
5.	2.5				polymerized		

TABLE 12 — CALCULATION OF p , $1/1-p$, $1/(1-p)^2$, K_2 and K_3 AT 200°C FOR POLYACETAL-FORMATION

Sl. No.	Heating time (hr)	C. V.	p	$1/1-p$	$1/(1-p)^2$	$K_2 \times 10^5$	$K_3 \times 10^5$
1.	0.5	56.2	0.068	1.073	1.151	2.421	4.153
2.	1.0	48.6	0.194	1.240	1.538	4.000	7.398
3.	1.5	44.0	0.270	1.397	1.952	4.389	8.727
4.	1.7				Polymerised		

here also they do not represent truly one kind of reaction or an overall type.

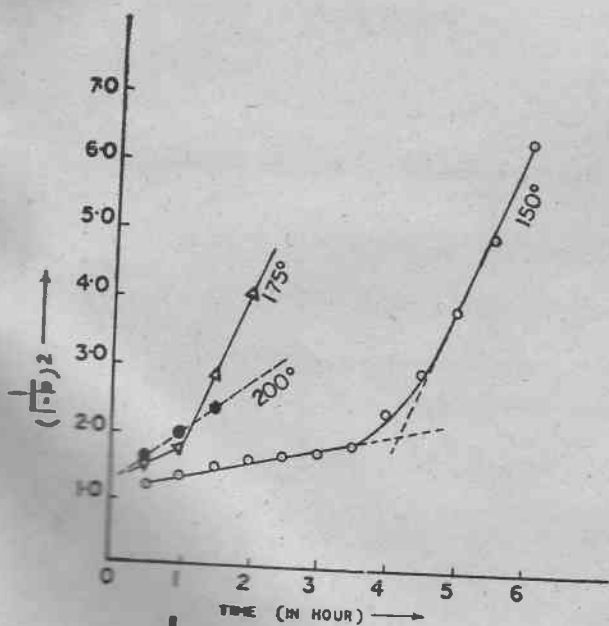


FIG. 4 $t, \frac{1}{(1-p)^2}$ CURVE FOR POLY-ESTERIFICATION

The velocity constants of the reactions, K_2 and K_3 , have also been calculated (Table 7 to 12). It will be evident from the values that during esterification, K_3 is almost constant upto 3.5 hr. while during polyacetal formation K_2 is almost constant upto 3.5 hr.

These would indicate that the esterification follows a third order reaction and is catalysed by the carboxyl groups of the shellac acids while the acetal formation follows a second order reaction being most probably catalysed also by the carboxyl groups.

ACKNOWLEDGEMENT

The authors are thankful to Dr. T. P. S. Teotia, Director, for his kind permission to publish the paper and to Dr. P. R. Bhattacharya and Dr. P. C. Gupta for their scrutiny of the manuscript.

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