

# Drying Rates of Polyamic Acid Solution Film under (i) Natural Convection and (ii) Induced Draft Drying Conditions

S. K. GUPTA, *Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Trivandrum-695022, India*

## Synopsis

Drying rate studies were carried out with polyamic acid solution synthesized in the laboratory in dimethyl acetamide solvent, with a view to determine the process design parameters of a continuous polyimide film casting machine. Studies reveal that drying under natural convection condition takes an unduly long time, whereas drying under induced draft/recirculation with partial recycle condition takes only  $\frac{1}{3}$  the time that of natural convection drying. Another important observation made was that under natural convection drying condition the initial adjustment period was too long and that the drying process was evenly spread over the initial adjustment, constant, and falling rates of the drying periods, whereas under induced draft condition drying mostly took place during the falling rate of drying period. The drying rate data obtained was used for generating the necessary process design, and operating parameters for a continuous polyimide film casting machine.

## INTRODUCTION

Polyamic acid was synthesized in the laboratory by an addition reaction between 4,4'-diaminodiphenyl ether and pyromellitic dianhydride in dimethyl acetamide solvent medium.<sup>1-4</sup> The resulting 10% solution of polyamic acid had an inherent viscosity of 2.5 dL/g and a bulk viscosity of 25000 cP at 28°C. This polyamic acid solution is cast into film on a moving polished stainless steel belt by a solution casting technique.<sup>5</sup> The belt is enclosed in a hot chamber maintained at 95–100°C. A constant nitrogen blanket is maintained inside the chamber. About 75% of the solvent is evaporated off from this polyamic acid solution film to make it self-supporting, enabling it to be taken up on a set of rollers enclosed in another hot chamber maintained at 300°C. A nitrogen blanket is maintained inside the second chamber also. Here polyamic acid film is converted into polyimide film by thermal dehydration. This film is used as major thermal and electrical insulation material in high power electric motors and for several other aerospace applications.

In this paper, results on drying rate studies carried out with polyamic acid solution film, to evaporate off 75% of the solvent in order to make the film self-supporting, are reported. The results obtained enabled the determination of necessary process design parameters for a continuous polyimide film casting machine and also the operating parameters during film formation.

## EXPERIMENTAL

Drying rate studies were carried out under (i) natural convection and (ii) induced draft with partial recycle conditions. For natural convection drying a  $1 \times 1 \times 1$  ft. oven was used and for drying under induced draft a  $2\frac{1}{2} \times 2\frac{1}{2} \times 2\frac{1}{2}$  ft. oven fitted with a recirculation fan was used. The latter oven had the provision to vent out part of the hot gases, thus enabling partial recycle condition inside the oven. Temperature in the ovens was adjusted at 95–100°C and a nitrogen blanket was achieved inside the ovens by a steady gas flow rate of 4 L/min.

The weighed quantity of polyamic acid solution was spread uniformly over two clean, dry glass plates. These plates with polyamic acid solution film were placed inside the two ovens, respectively. Weight loss was noted from each plate at regular intervals till about 80–85% solvent evaporated off. The area of the dried films was determined by a graphical method. The weight loss data and surface area of the film were computed to obtain the rate of drying  $N$  (g solvent evaporated/min  $m^2$ ). Rates-of-drying data were plotted against the solvent content of the polymer during different stages of drying operation. These plots were used for working out drying time for drying larger quantities of polyamic acid solution in a continuous film casting machine under two different drying conditions. Design parameters of a typical continuous film casting machine available commercially were considered for working out drying times.

## RESULTS AND DISCUSSION

Drying test data obtained during laboratory experiments conducted under two different drying conditions have been tabulated in Tables I and II and plotted as solvent content (g solvent/g dry solid) against time (min) Figures 1 and 2. These data were computed to obtain the rate of drying, expressed as  $N$  (g solvent evaporated/min  $m^2$ ) and tabulated in Tables III and IV and have been plotted against solvent content, as shown in Figures 3 and 4. These plots have been used for determining drying time for drying larger batches of polyamic acid solution in a continuous polyimide film casting machine under similar drying conditions. This determined the suitability of the design parameters for a given machine and also the correspondingly obtainable operating parameters. Alternatively, for a given set of operating parameters, design details for the casting machine can be specified.

TABLE I  
Experimental Drying Test Data for Natural Convection Drying of Polyamic Acid Solution<sup>a</sup>

Serial no.	Time (min)	X (g solvent/g dry solid)
1	0	9.0
2	15	8.71
3	30	8.01
4	45	7.19
5	60	6.02
6	75	4.85
7	90	3.83
8	105	2.91

<sup>a</sup> Temperature = 95–100°C,  $N_2$  flow rate = 4 L/min.

TABLE II  
Experimental Drying Test Data for Induced Draft Drying of Polyamic Acid Solution<sup>a</sup>

Serial no.	Time (min)	X (g solvent/g dry solid)
1	0	9.0
2	10	6.77
3	20	5.01
4	30	3.76
5	40	2.80
6	50	2.13
7	60	1.61
8	70	1.31

<sup>a</sup> Temperature = 95–100°C, N<sub>2</sub> flow rate = 4L/min.

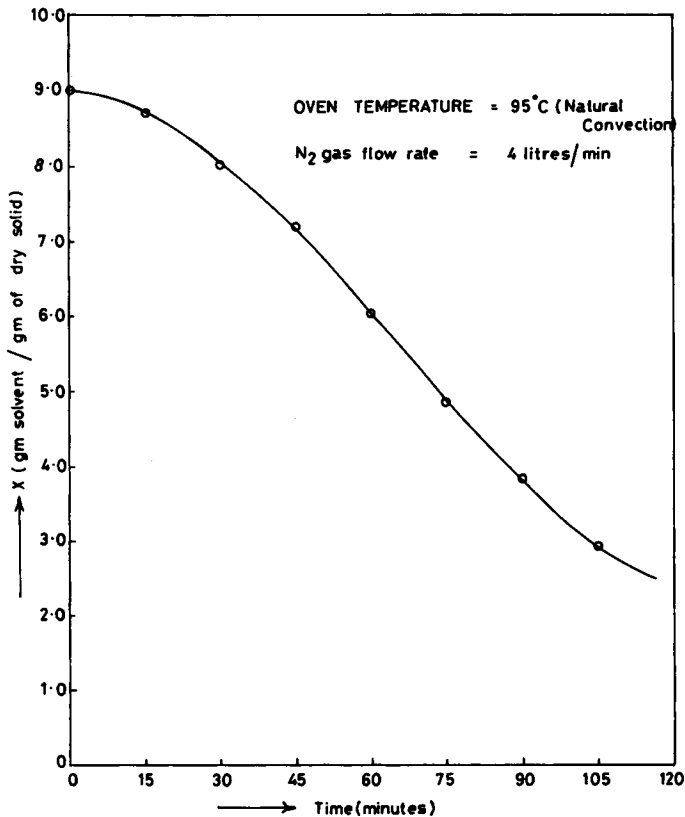


Fig. 1. Solvent content of polyamic acid solution as a function of time under natural convection drying condition.

### DRYING TIME CALCULATION ON A TYPICAL CONTINUOUS POLYIMIDE FILM CASTING MACHINE UNDER NATURAL CONVECTION DRYING CONDITION

**Machine Parameters.** Film casting length of polished stainless steel belt = 3.7 m; casting width = 300 mm; feeder lip clearance = adjustable (let

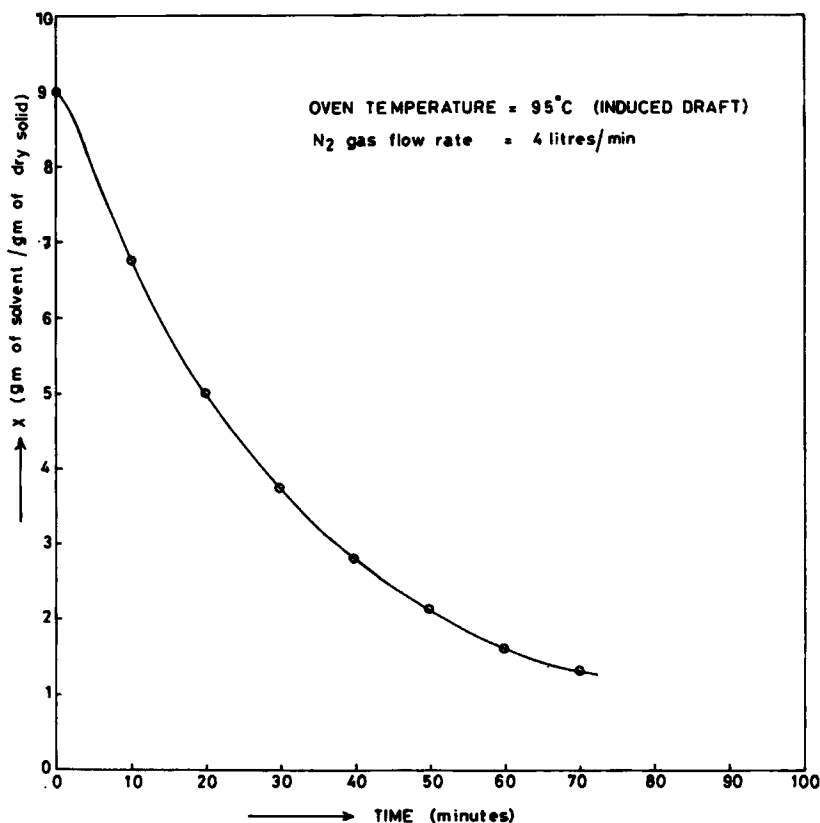


Fig. 2. Solvent content of polyamic acid solution as a function of time under induced draft with partial recirculation drying condition.

the lip clearance be 1 mm in the first instance); volume of the polyamic acid solution used for casting =  $370 \times 30 \times 0.1 \text{ cm} = 1110 \text{ cm}^3$ ; weight of the polyamic acid solution used for casting = 1110 g (density = 1 g/cc); weight of dry solid ( $L_s$ ) = 111 g; area of the film exposed for drying =  $3.7 \times 0.3 \text{ m} = 1.11 \text{ m}^2$ ; weight of dry solid per unit area =  $L_s/A = 111 \text{ g}/1.11 \text{ m}^2 = 100 \text{ g dry solid}/\text{m}^2$ . For 75% of the solvent evaporation from polyamic acid solution film, drying takes place from  $X_1 = 9.0 \text{ g solvent}/\text{g dry solid}$  to  $X_2 = 2.25 \text{ g solvent}/\text{g dry solid}$ .

From the drying-rate curve (Fig. 3) it is seen that the drying process involves initial-adjustment-, constant-, and falling-rate periods. It is also observed that drying during initial-adjustment- and falling-rate periods occurs under conditions of changing  $N$ .

By definition,<sup>6</sup>

$$\text{rate of drying } N = -\frac{L_s}{A} \cdot \frac{dX}{d\theta}$$

Rearranging and integrating over the time interval while the solvent content changes from its initial value  $X_1$  to its final value  $X_2$ ;

TABLE III  
Rate of Drying Computed from Figure 1<sup>a</sup>

Serial no.	X (g solvent/ g dry solid)	$\Delta X/\Delta \theta$ (g solvent evaporated/ min g dry solid)	N, rate of drying (g evaporated /min m <sup>2</sup> ), (L <sub>s</sub> /A)· ( $\Delta X/\Delta \theta$ )
1	8.95	0.013	2.8
2	8.82	0.022	4.7
3	8.62	0.042	9.06
4	8.37	0.042	9.06
5	8.12	0.056	12.08
6	7.87	0.067	14.08
7	7.62	0.056	12.08
8	7.25	0.067	14.45
9	6.75	0.074	15.96
10	6.25	0.083	17.9
11	5.75	0.074	15.96
12	5.25	0.074	15.96
13	4.75	0.074	15.96
14	4.25	0.074	15.96
15	3.75	0.067	14.45
16	3.37	0.067	14.45
17	3.12	0.067	14.45
18	2.87	0.048	10.35
19	2.62	0.037	7.98

<sup>a</sup> L<sub>s</sub>/A = 4.53 g/0.021 m<sup>2</sup> = 215.71 g dry solid/m<sup>2</sup>.

$$\theta = \int_0^{\theta} d\theta = \frac{L_s}{A} \int_{X_2}^{X_1} \frac{dX}{N}$$

Thus, the time of drying during the initial-adjustment- and falling-rate periods can be calculated by graphically integrating the area under a curve plotted against 1/N as ordinate and X as abscissa, the data for which are obtained from the rate-of-drying curve (Fig. 3) and tabulated in Tables V and VI and plotted in Figure 5.

**Drying Time for Initial Adjustment Period.** Area under the curve 1/N vs. X (from X<sub>1</sub> = 9.0 to X<sub>c1</sub> = 6.75) = 0.21 units (Fig. 5). Therefore, θ<sub>i</sub> = L<sub>s</sub>/A × 0.21 = 100 × 0.21 = 21 min.

**Drying Time for the Falling-Rate Period.** Area under the curve 1/N vs. X (from X<sub>c2</sub> = 4.25 to X<sub>2</sub> = 2.25) = 0.1825 units (Fig. 5). Therefore, θ<sub>f</sub> = 100 × 0.1825 = 18.25 min.

**Drying Time for the Constant-Rate Period.**

$$\theta_c = \frac{L_s(X_{c1} - X_{c2})}{AN_c} = \frac{100(6.75 - 4.25)}{15.95} = 15.7 \text{ min}$$

$$\text{total drying time} = \theta_i + \theta_c + \theta_f = 54.95 \text{ min}$$

TABLE IV  
Rate of Drying Computed from Figure 2<sup>a</sup>

Serial no.	X (g solvent/ g dry solid)	$\Delta X/\Delta\theta$ (g solvent evaporated/min g dry solid)	N, rate of drying, (g evaporated/min m <sup>2</sup> ) ( $L_s/A$ ) · ( $\Delta X/\Delta\theta$ )
1	8.875	0.125	32.28
2	8.62	0.25	64.56
3	8.37	0.333	86.00
4	8.12	0.333	86.00
5	7.875	0.25	64.56
6	7.625	0.25	64.56
7	7.25	0.222	57.33
8	6.75	0.222	57.33
9	6.25	0.182	47.0
10	5.75	0.182	47.0
11	5.25	0.154	39.8
12	4.75	0.133	34.34
13	4.25	0.125	32.3
14	3.75	0.125	32.3
15	3.25	0.095	24.53
16	2.75	0.08	20.7
17	2.375	0.067	17.3
18	2.125	0.063	16.3
19	1.875	0.056	14.5
20	1.625	0.04	10.33
21	1.375	0.028	7.17

<sup>a</sup> ( $L_s/A = 3.68 \text{ g}/0.01425 \text{ m}^2 = 258.25 \text{ g dry solid}/\text{m}^2$ .)

### DRYING TIME CALCULATIONS FOR INDUCED DRAFT WITH PARTIAL RECYCLE DRYING CONDITION

**Basis.** As considered earlier,  $L_s/A = 100 \text{ g dry solid}/\text{m}^2$ . From drying rate curve (Fig. 4) it is seen that the drying process again involves all three drying periods, and during initial-adjustment- and falling-rate periods it occurs under conditions of changing  $N$ . Therefore,

$$\theta = \frac{L_s}{A} \int_{X_2}^{X_1} \frac{dX}{N}$$

Drying time during these two periods is calculated by graphically integrating the area under the curve plotted against  $1/N$  as ordinate and  $X$  as abscissa, the data for which are obtained from the rate-of-drying curve (Fig. 4) and tabulated in Tables VII and VIII and plotted in Figure 6.

**Drying Time for Initial Adjustment Period.** Area under the curve  $1/N$  vs.  $X$  (from  $X_1 = 9.0$  to  $X_{c1} = 8.37$ ) = 0.015375 units (Fig. 6). Therefore,  $\theta_i = (L_s/A) \times 0.015375 = 100 \times 0.015375 = 1.54 \text{ min}$ .

**Drying Time for the Falling-Rate Period.** Area under the curve  $1/N$  vs.  $X$  (from  $X_{c2} = 8.12$  to  $X_2 = 2.25$ ) = 0.1675 units (Fig. 6). Therefore,  $\theta_f = 16.75 \text{ min}$ .

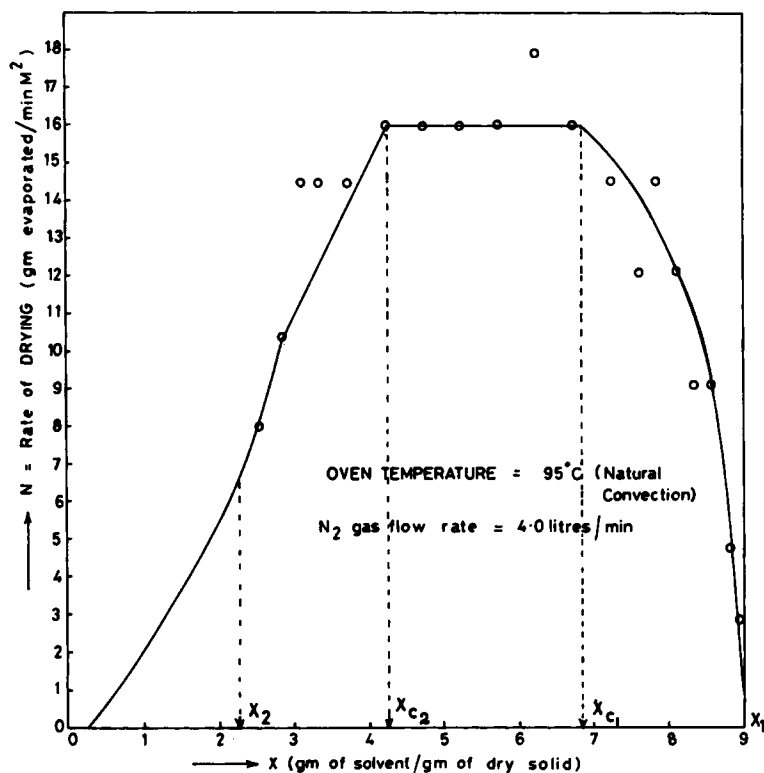


Fig. 3. Rate of drying curve under natural convection drying condition (polyamic acid solution).

### Drying Time for the Constant-Rate Period.

$$\theta_c = \frac{L_s(X_{c1} - X_{c2})}{AN_c} = \frac{100(8.37 - 8.12)}{86}$$

$$= 0.3 \text{ min}$$

$$\text{total drying time} = 18.59 \text{ min}$$

From the drying times obtained under two different drying conditions it is observed that drying of polyamic acid solution film under the induced-draft drying condition is three times faster than that under the natural convection drying condition. Such reduced drying time under the induced-draft drying condition enables reduction in the requirement of belt length, overall machine size, and the heating capacity of a continuous film casting machine. It could thus be beneficial to operate a continuous film casting machine in induced draft mode. These drying times, as worked out above, also enable determining the operating speed of the belt, the extrusion speed of the feeder, and the capacity of the plant. The extrusion speed of the feeder should always be equal to the belt speed.

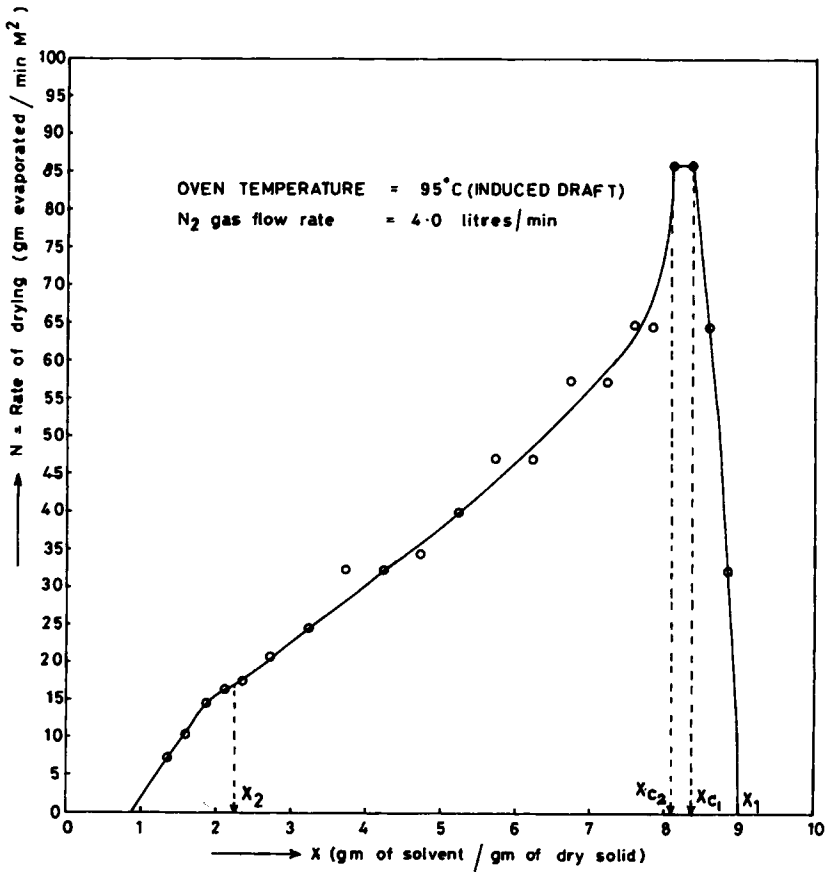


Fig. 4. Rate of drying curve under induced draft with partial recirculation drying condition (polyamic acid solution).

TABLE V  
1/N vs. X for Initial Adjustment Period

X	N	1/N
8.95	2.8	0.357
8.9	3.9	0.256
8.75	6.4	0.156
8.5	10.0	0.1
8.0	12.65	0.079
7.5	14.5	0.069
7.0	15.65	0.064
6.75	15.95	0.063

A further observation made is that under natural convection drying operation, drying process is evenly spread over the three drying periods, whereas under the induced-draft condition the drying process quickly passes over to the falling rate of drying period, and drying mostly takes place during this period (Figs. 3 and 4).



TABLE VI  
 $1/N$  vs.  $X$  for the Falling Rate Period

$X$	$N$	$1/N$
4.25	15.95	0.063
4.0	14.9	0.067
3.75	13.9	0.072
3.5	12.9	0.078
3.0	10.9	0.092
2.75	9.4	0.106
2.5	7.7	0.130
2.25	6.5	0.154

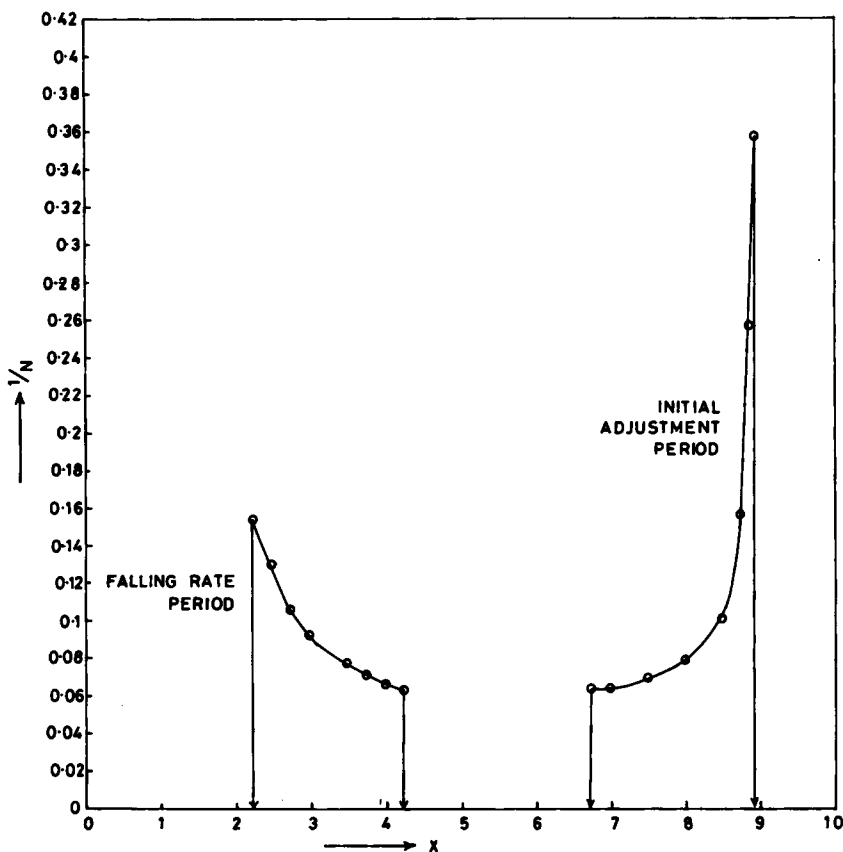


Fig. 5. Solvent content of polyamic acid solution as a function of inverse of rate of drying under natural convection drying condition.

### TYPICAL CALCULATION OF OPERATING PARAMETERS FOR A GIVEN MACHINE USED UNDER INDUCED DRAFT DRYING CONDITION

Casting length of belt = 370 cm, slit clearance = 1 mm:  
 drying time = 19 min (as calculated earlier)  
 belt speed = 370 cm/19 min  $\approx$  20 cm/min

TABLE VII  
1/N vs. X for the Initial Adjustment Period

X	N	1/N
9.0	10	0.1
8.9	30	0.033
8.8	45	0.022
8.75	50	0.02
8.7	57	0.0175
8.5	77.5	0.0129
8.37	86.0	0.0116

TABLE VIII  
1/N vs. X for the Falling-Rate Period

X	N	1/N
8.12	86	0.0116
8.0	73.5	0.0136
7.75	65.5	0.0153
7.5	61.5	0.0163
7.0	56.0	0.0179
6.5	51.0	0.0196
6.0	46.5	0.0215
5.5	42.0	0.0238
5.0	37.5	0.0266
4.5	34.0	0.0294
4.0	30.0	0.0333
3.5	26.25	0.038
3.0	22.5	0.044
2.5	18.5	0.054
2.25	16.5	0.0606
2.0	14.5	0.069

drum diameter = 50 cm

rpm of drum =  $20/\pi \times 50 \approx \frac{1}{8} = 0.125$

extrusion speed = 20 cm/min

capacity of the plant = 12.0 kg/day of 100  $\mu$ m thick Polyimide film

For varying feeder slit clearance belt speed adjustments are listed in Table IX (belt length available for casting film = 3.7 m).

For varying extrusion speeds, belt length requirements are listed in Table X (slit clearance = 1 mm).

## CONCLUSION

Process design and operating parameters for a continuous film casting machine can be specified on the basis of laboratory drying test data obtained for the polymer solution under consideration. It is found that induced draft drying is beneficial over natural convection drying in terms of reduced drying time, belt length, overall size, and heating capacity of the machine.

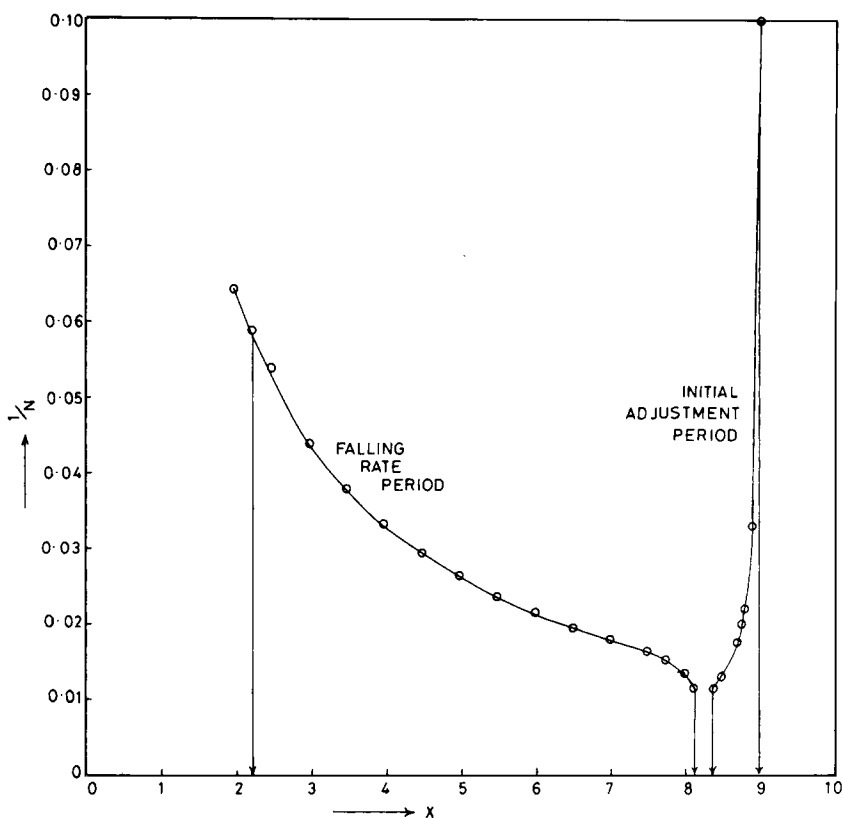


Fig. 6. Solvent content of polyamic acid solution as a function of inverse of rate of drying under induced draft with partial recycle drying condition.

TABLE IX

Slit clearance (mm)	$L_s/A$ (g dry solid/m <sup>2</sup> )	Drying time (min)	Belt speed (cm/min)	Drum (rpm)	Capacity of the plant (kg/day)
1	100	19	20	0.125	12.0
0.75	75	14.25	26.66	0.17	12.0
0.50	50	9.5	40.0	0.25	12.0
0.25	25	4.75	80.0	0.50	12.0

TABLE X

Extrusion speed (cm/min)	Belt speed (cm/min)	Drum (rpm)	Belt length (m)	Capacity of the plant (kg/day)
20	20	0.125	3.7	12.0
40	40	0.25	7.4	24.0
60	60	0.375	11.1	36.0
80	80	0.5	14.8	48.0
100	100	0.625	18.5	60.0
120	120	0.75	22.2	72.0
160	160	1.0	29.6	96.0

The author would like to thank Dr. S. Someswara Rao for his helpful comments during the preparation of this manuscript.

### APPENDIX: NOTATION

- A drying surface, square meter  
 $L_s$  weight of dry solid in a batch (g)  
 $N$  rate of drying (g solvent evaporated/h m<sup>2</sup>)  
 $N_c$  constant rate of drying (g solvent evaporated/h m<sup>2</sup>)  
 $X$  solvent content of the solid (g solvent/g dry solid)  
 $X_1$  solvent content of the solid at start of drying operation (g solvent/g dry solid)  
 $X_2$  solvent content of the solid at the end of drying operation (g solvent/g dry solid)  
 $X_{c1}$  critical solvent content at the point where initial adjustment period ends (g solvent/g dry solid)  
 $X_{c2}$  critical solvent content at the point where the falling rate of the drying period starts (g solvent/g dry solid)  
 $\theta$  time (min)  
 $\theta_c$  drying time for the constant rate of the drying period (min)  
 $\theta_f$  drying time for the falling rate of the drying period (min)  
 $\theta_i$  drying time for the initial adjustment period (min)  
 $\Delta$  difference

### References

1. C. E. Sroog, *J. Polym. Sci., C*, **16**, 1191 (1967).
2. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Oliver, *J. Polym. Sci. A*, **3** 1373 (1965).
3. R. Ikeda, *J. Polym. Sci. B*, **4**, 353 (1966).
4. W. M. Edwards, U.S. Pat. 3,179,614 (1965).
5. A. H. Frazer, *High Temperature Resistant Polymers*, Wiley-Interscience, New York (1968).
6. Robert E. Treybal, *Mass Transfer Operations*, McGraw-Hill, New York (1968).

Received October 21, 1985

Accepted November 15, 1985