Effect of Turnover Rate on the Change of Concentration of an Unstable Compound in a Dip Coating Bath

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The effect of turnover rate on the change of concentration of unstable (degradable) compounds in a dip coating bath during a continuous coating process was theoretically calculated as a function of the degradation rate of the compound. It is assumed that the bath is replenished by the same coating material as that in the original bath to maintain the volume of the material in the bath constant.

The results show that the fraction of the unstable compound in the bath at the end of the nth day is given by

$$C_n = X^n + \frac{1}{t}\left(\frac{1-X^n}{1-X}\right)$$

where t is the number of days for one turnover and

$$X = \left(1-\frac{1}{t}\right)P$$

where P is the fraction of the compound remaining undegraded in the bath per day.

The equilibrium fraction of the compound after infinite coating days is given by

$$\lim_{n\to\infty} C_n = \frac{1}{t+P-Pt}$$

The concentration of the compound in the replenishing material (C_r) to maintain the original concentration in the bath (C_o) constant is given by

$$C_r = C_o\,(t + P - Pt)$$

INTRODUCTION

The effect of turnover rate on the change of solid content in a dip coating bath due to evaporation of solvents was theoretically calculated by the author in a previous paper.[1] The present paper deals with the effect of turnover rate on the change of concentration of unstable (degradable) compounds due to degradation during a continuous dip coating process.

Unstable compounds are often contained in a dip coating bath. The author found that cellulose derivative polymer thickeners degrade chemically[2] and mechanically[3,4] in aqueous solutions containing chromic acid and, thus, the viscosity decreases with time. It is well known that organosilicone surfactants degrade in acidic or alkaline aqueous solutions and, thus, the surface tension changes with time.[5]

It is important to understand the change in the material balance in a dip coating bath containing unstable compounds during a continuous coating process to control the quality. However, no systematic work has been found on the change of the concentration of unstable compounds in a dip coating bath during the coating process.

In the present work, theoretical equations were derived for the change of the concentration of unstable compounds in the bath as functions of the degradation rate of the compounds and turnover rate.

COMPUTATION

Change of the Concentration of Unstable Compounds in a Dip Coating Bath with Time

It is assumed that the bath is replenished at the end of each day to maintain the volume in the bath constant, and one turnover is accomplished in t days. Then, the fraction of the material removed by coating per day is $1/t$, and the fraction that remained in the bath is $1 - 1/t$. Letting the fraction of the unstable compounds that remained undegraded per day P (= 1 – degradation rate/day), the fraction of the compounds that remained at the end of the first day is

$$\left(1-\frac{1}{t}\right)P$$

Since the same amount of fresh coating material as that removed by coating ($1/t$) is replenished at the end of each day to maintain the volume constant, a total amount of the compound in the bath at the end of the first day is given by

$$C_1 = \left(1-\frac{1}{t}\right)P + \frac{1}{t}$$

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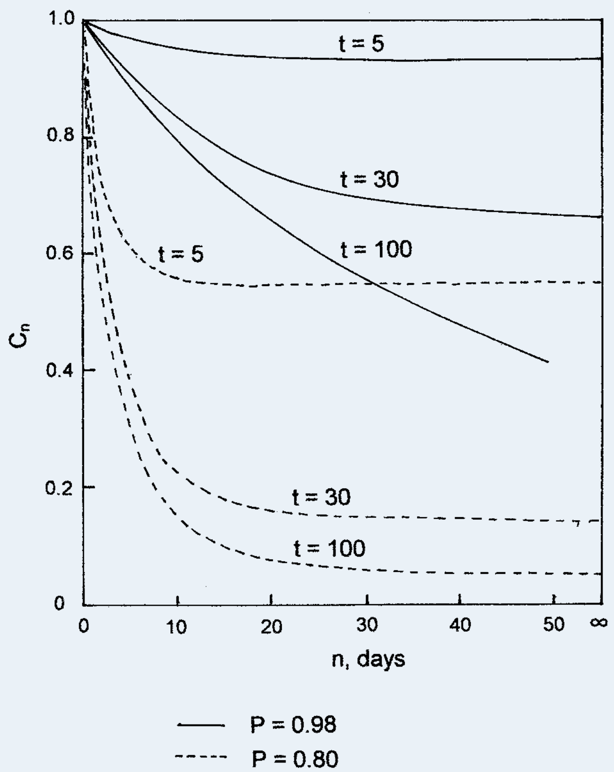

Figure 1—Change of concentration of unstable compound with time in dip-coating bath.
________ P= 0.98: Degradation rate, 2%/day
– – – – P= 0.80: Degradation rate, 20%/day

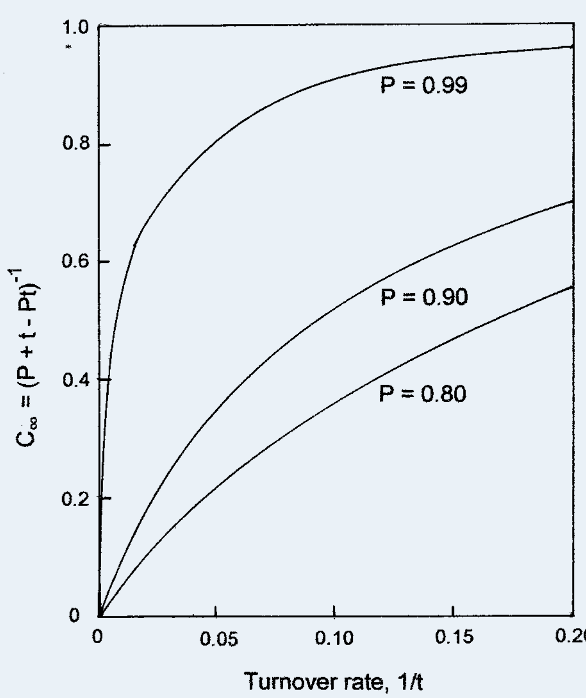

Figure 2—Change of equilibrium concentration with degradation rate.

The fraction of the compound at the end of the second day is

$$C_2 = C_1\left(1-\frac{1}{t}\right)P + \frac{1}{t}$$

Letting $\left(1-\frac{1}{t}\right)P = X$ and $\frac{1}{t} = Y$

$$C_1 = X + Y$$
$$C_2 = C_1X + Y = (X + Y)\,X + Y = X^2 + XY + Y.$$

In the same manner, the amount of the compound in the bath at the end of the nth day, C_n, is given by

$$C_n = X^n + Y\left(X^{n-1} + X^{n-2} + \ldots + X^0\right) = X^n + Y\left(\frac{1-X^n}{1-X}\right) \quad (1)$$

since $X < 1$.

Substituting X and Y by t and P,

$$C_n = \frac{(1-1/t)^n P^n (t-1)(1-P) + 1}{t + P - Pt} \quad (2)$$

Equilibrium Concentration of the Compound

The concentration of the compound after infinite days of coating, C_∞, is calculated by the following equation:

$$\lim_{n\to\infty} C_n = \left\{\left\{X^n + Y\left(\frac{1-X^n}{1-X}\right)\right\}\right\} = \frac{Y}{1-X} \quad (3)$$

Since $\lim_{n\to\infty} X^n = 0$

Substituting X and Y by t and P,

$$C_\infty = \frac{1}{t + P - Pt} \quad (4)$$

Concentration of the Compound in Replenishing Coating Material to Maintain the Concentration in the Bath Constant

The concentration of the unstable compound in the replenishing material should be higher than that in the original bath to maintain the concentration constant during the coating process. If the concentration in the original bath is C_o, and the concentration in the replenishing material is C^r, the concentration at the end of the nth day is given by

$$C_n = C_o X^n + \frac{C_r}{t}\left(\frac{1-X^n}{1-X}\right) \quad (5)$$

The equilibrium concentration after infinite days of coating is given by

$$\lim_{n\to\infty} C_n = \frac{C_r}{t + P - Pt} \quad (6)$$

Since $\lim_{n\to\infty} X_n = 0$

When $P = 1$ (no degradation)

$\lim_{n\to\infty} C_n = C_r$

The difference between the concentration of the compound at the nth day and the concentration at the $(n + 1)$ day is calculated by

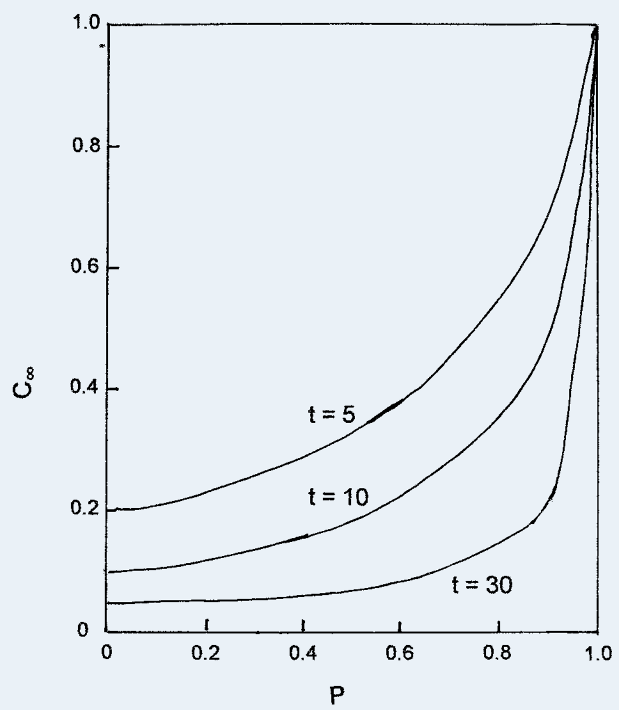

Figure 3—Change of equilibrium concentration with degradation rate of the compound for three different turnover rates.

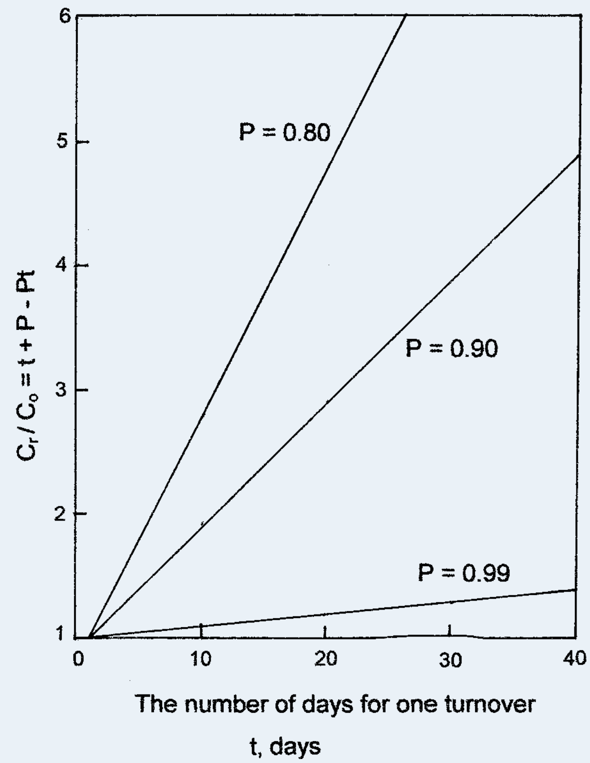

Figure 4—Concentration of unstable compound in replenishing material needed to maintain the concentration constant vs. the number of days for one turnover.

$$C_{n+1} - C_n = \left\{ C_o X^{n+1} + \frac{C_r}{t}\left(\frac{1 = X^{n+1}}{1 - X}\right)\right\} - \left\{ C_o X^n + \frac{C_r}{t}\left(\frac{1 - X^n}{1 - X}\right)\right\} \quad (7)$$

$$= X^n \left\{ C_o (X - 1) + \frac{C_r}{t} \right\} \quad (8)$$

In order to make the difference 0 during the coating process to maintain the concentration in the bath constant,

$$C_o (X - 1) + \frac{C_r}{t} = 0 \quad (9)$$

Therefore,

$$\frac{C_r}{C_o} = (1 - X)t = (1 - P)t + P \quad (10)$$

Equation (10) indicates that the ratio of C_r / C_o increases linearly with t for a given compound.

RESULTS AND DISCUSSION

The results are shown in *Figures* 1-4.

Figure 1 shows the change in the concentration of the unstable compound in the bath with time for two different compounds of different degradation rates: P = 0.98 (2% degradation/day) and P = 0.8 (20% degradation/day). The concentration of the compound in the bath decreases more rapidly as the degradation rate of the compound decreases (P increases) and turnover rate decreases (t increases).

Figure 2 shows the change of the equilibrium concentration with turnover rate ($1/t$). It shows that the equilibrium concentration can be maintained at a high level by increasing the turnover rate even if the degradation rate is high.

Figure 3 shows the relation between the equilibrium concentration and the degradation rate of the compounds. It indicates that the equilibrium concentration increases as the degradation rate increases (P decreases).

Figure 4 shows the effect of turnover rate and the degradation rate on the concentration of the compound in the replenishing material (C_r) needed to maintain the original concentration (C_o) in the bath. It shows that the concentration of the compound in the replenishing material should be increased as the turnover rate decreases (t increases), and the degradation rate increases (P decreases). C_r/C_o increases linearly as the number of days for one turnover increases. Thus, if it takes 30 days for one turnover (t = 30) and the degradation rate of the compound is 10% per day (P = 0.9), the concentration in the replenishing material should be increased about four times higher than the original concentration to prevent reduction of the concentration in the bath as shown in *Figure* 4.

References

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