An Automatic Concentration Control of the Neutralization Bath in Wet Processing

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Abstract

Most wet processes can be more safely and more economically carried out with the aid of the control techniques of today.

In this paper, we theoretically analyzed the behavior of neutralization process in wet processing using well known mass transfer equations for the purpose of automatic controlling its acid concentration.

Based on this analysis, feedback control was applied to a real neutralization bath concentration in mercerization processing by means of automatic titration method.

As the result, we obtained satisfactory data for the practical process by this control method.

KEY WORDS: WET FINISHING, MASS TRANSFER, CONTROL SYSTEMS, RIC ANALYSIS, CELLULOSE, SODIUM HYDROXIDE, ACID SOLUTIONS, CONCENTRATION

1. Introduction

Caustic solution is often used in chemical treatments (e.g., mercerizing) of cotton fabrics. However, having good affinity for cotton-constituent cellulose, the caustic soda cannot be completely removed by washing. To wash out the residuary alkaline substance the treated cotton fabric is passed through the acid solution for neutralizing. This acid solution bath is referred to as "a neutralization bath."

Controlling the concentration of acid solution in the neutralization bath is very important to obtain high quality products but there have no published works on the subject, except some reports dealing with the concentration and temperature control of caustic soda solution.[1]

This paper analyzes the neutralization process and finds a concrete method to control the concentration of neutralization acid solution.

2. Analysis of Neutralization Process

The neutralization process mentioned here is such as Fig.1.

The cotton fabric treated by caustic soda solution is, after washing, guided to sulphuric acid solution bath to neutralize the residuary caustic substance in the structure of cotton fabric, which is washed out in the next washing bath.

The neutralization reaction in the bath is $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$. Namely, caustic soda is replaced with surplus sulphuric acid that has not affinity for cellulose and easily washed out by following washing.

Now to analyze the above neutralization process using the following nomenclatures:

- Fabric thickness: $2\delta$
- Normal solution concentration of caustic soda in the structure of the cotton fabric that is brought into the neutralization bath: $C_Y$
- Normal solution concentration of sulphuric acid in the structure of the cotton fabric: $C_H$
- Transfer efficiency of sulphuric acid solution into the fabric: $D$

As the treated fabric enters into the neutralization bath,
the sulphuric acid solution in the bath penetrates into the structure of the fabric reacting against the caustic soda left in the fabric. Since this chemical reaction is of a neutralization which is instantaneous in reaction, the time for it can be neglected.

Fortunately, a well-known mass transfer equation\(^2\) can be applied for the sulphuric acid solution concentration \(C_H\) penetrating the structure of the cotton fabric.

\[
\frac{\partial C_H}{\partial t} = D \frac{\partial^2 C_H}{\partial x^2} \tag{1}
\]

where \(t\) is time and \(x\) is the distance from the fabric surface to the inside of the fabric.

Assuming that the point \(x'\) in Fig. 2 is a reaction surface of meeting of caustic soda and sulphuric acid, then the sulphuric acid solution concentration \(C_H\) and caustic soda solution concentration \(C_N\) are both considered to become 0 by neutralization reaction. As the sulphuric acid solution penetrates into the structure of the fabric, the reaction surface moves. If the distance of this movement in time \(dt\) is \(dx'\), the following equation will be obtained from Fig. 2:

\[
MN = \frac{\partial C_H}{\partial t} dt = - \frac{\partial C_H}{\partial x} dx' \tag{2}
\]

In the above relation, it is considered that the sulphuric acid amount in the neutralization bath is very large compared to the caustic soda in the structure of the fabric, and that the movement rate of sulphuric acid to the fabric surface in the neutralization bath is higher because of the agitation by the fabric itself than the movement rate into the structure of the fabric. So that, the concentration of sulphuric acid solution on the fabric surface is always constant and equal to the concentration \(C\) in the bath. Under this condition, if the eq. (1) is solved, the eq. (3) is obtained.

\[
C_H = A + Berf \left[ \frac{x}{2\sqrt{Dt}} \right] \tag{3}
\]

where \(A\) and \(B\) are constants determined by the initial conditions and boundary conditions. And \(\partial C_H/\partial t, \partial C_H/\partial x\) are calculated by differential eq. (3) by \(t\) and \(x\) and substituted into eq. (2) as follows:

\[
\frac{dx'}{dt} = - \frac{\partial C_H}{\partial t}/\frac{\partial C_H}{\partial x} = \frac{x'}{2t} \tag{4}
\]

Then this is integrated as follows:

\[
x' = 2\sqrt{\frac{t}{D}} \tag{5}
\]

where \(\beta\) is an integration constant.

The total time of movement of the reaction surface \(x'\), i.e., the time \(t_e\) during which all the caustic soda in the fabric is replaced by sulphuric acid expelled by the reaction from the both sides of the fabric, is

\[
t_e = \frac{\partial t}{4\beta} \tag{6}
\]

From the equation it is clear that the time of movement of the reaction surface is proportional to the square of the fabric thickness \(d\). If \(\beta\) is known, the time is in turn known. To calculate \(A, B\) in eq. (3) and this \(\beta\), we use as initial conditions and boundary conditions the following;

(i) \(x=0, t>0, C_H = C\)

(ii) \(x=x', t>0, C_H = C_N = 0\)

and, we use a mass balance equation at reaction surface \(x'\):

\[
D \frac{\partial C_H}{\partial x} \mid_{x'} + C_N \frac{dx'}{dt} = 0 \tag{7}
\]

We obtain from eq. (3) under such initial and boundary conditions:

\[
A = C
\]

\[
B = -CN\sqrt{\frac{\pi\beta}{D}} \exp \left( \frac{\beta}{D} \right) \tag{8}
\]

Accordingly, \(\beta\) is obtained by substituting eq. (8) into eq. (3) as follows:

\[
\sqrt{\frac{\pi\beta}{D}} \exp \left( \frac{\beta}{D} \right) erf \left( \frac{\beta}{D} \right) = \frac{C}{C_N} \tag{9}
\]

In this way, if \(\beta\) is determined, \(t_e\) can be obtained as a function of the concentration in the bath from eqs. (6) and (9) because \(C\) is the concentration of sulphuric acid solution in the bath. This \(t_e\) is the time until the fabric which entered into the neutralization bath enters into the next washing bath or it is a value to determine the concentration of the sulphuric acid solution in the neutralization bath.

It is hard to analytically calculate \(\beta\) from eq. (9). So the relation between \(\beta/D\) and \(C/C_N\) are illustrated in Fig. 3. From Fig. 3 we calculate the value of \(\beta\).

Transfer efficiency \(D\) can be regarded as \(D = 10^{-5} [cm^2/sec]\) even if it is affected slightly by temperature.

If the fabric thickness is 200 micron and according
The relation between $t_e$ and $C/C_N$ is as shown in Fig. 4.

For numeric example, the operational data of the actual mercerizing process is substituted in eq. (9), $t_e = 7 \text{ [sec]}$ is obtained when $C/C_N = 0.5$. This is a proof that the time between when entering into the neutralization bath and when entering into the washing bath shall be over 7 secs. If the time between them is above 7 secs, the caustic soda in the fabric can be completely eliminated by determining the concentration $C$ of the neutralization bath since $C/C_N = 0.5$.

3. Dynamic Characteristics of Concentration in Neutralization Bath

Based on above idea, we try to obtain a basic equation to control the concentration of acid solution in the neutralization bath.\(^{[31]}\)

The solution amount per length of the fabric of unit width brought in the neutralization bath: $p \text{ [l/m]}

The solution amount per length of the fabric of unit width brought out from the neutralization bath: $q \text{ [l/m]}

Normal concentration of acid supplied to the neutralization bath: $C_i \text{ [N/l]}

Acid solution amount supplied to the neutralization bath: $w \text{ [l/min]}

The capacity of neutralization bath: $V \text{ [l]}

Running speed of the fabric: $v \text{ [m/min]}

Now if $\alpha$ of caustic soda amount brought into the neutralization bath is consumed, the following equation is obtained from the balance of the concentration:

$$\frac{d}{dt} (VC) = wC_i - \alpha pCNv - qCv$$

Then, from the mass balance,

$$\frac{dV}{dt} = w + \alpha pv - qv$$

If the solution level remains constant the left side of the equation (11) is 0. Naturally,

$$w + \alpha pv - qv = 0$$

Since $p$ is constant by a squeezing ratio of the mangle and $C_i$ is constant by a concentration of supplied sulphuric acid solution, the deviation from the steady state is presented by

$$C = C_i + \Delta C$$

$$q = q_i + \Delta q$$

$$w = w_i + \Delta w$$

$$CN = CNS + \Delta CN$$

Here the items with suffices $i$ is a stationary value and the items with $\Delta$ are deviation from the stationary values. Substituting eqs. (12) and (13) into eq. (10),

$$V \frac{d\Delta C}{dt} = \left( C_i - C_N \right) \Delta w - \alpha p \Delta C_N v - q \Delta C v$$

Laplace-transforming the both sides of the eq. (14),

$$\mathcal{L}\{\Delta C(S)\} = \left( C_i - C_N \right) \Delta W(S) - \alpha p q_i \mathcal{L}\{C_N(S)\}$$

where $\Delta W(S)$ is a control quantity and $\Delta C_N(S)$ is considered as a disturbance due to caustic soda brought into by the fabric. From eq. (15) the time constant $T$ of this process is

$$T = \frac{V}{q_i v}$$

To consider of the feed back control of the concentration in the neutralization bath having the dynamic characteristics represented by eq. (15), a block diagram is shown in Fig. 5.

Where $C_0$ is a desired concentration of neutralization bath, and $G_c(S)$ is a transfer function of the controller.

The ratio $\alpha$ of caustic soda consumed in the neutralization bath can be calculated from its staying time of caustic soda in the bath eqs. (6) and (9). It is also possible by measurement.
Re-check Figs. 3 and 4 from the standpoint of control of the concentration, it is known the gradients of the graphs are reverse. For this reason, the larger \( \frac{C}{C_X} \) is in Fig. 3, the larger the variation of \( t_e \) due to variation of \( \beta \). On the contrary, in Fig. 4, if \( \beta \) is determined, the larger \( \frac{C}{C_X} \) the smaller the variation of \( t_e \). Accordingly, the efficiency of control is made better by the compensation-off between \( B/D \) in Fig. 3 and \( t_e \) in Fig. 4.

From this, it is said that the controller \( G_c(S) \) need not be of a high class. Considering time constant \( T \) is large value, cheap on-off controller will do enough.

It is clear from eqs. (15) and (16) that the larger the time constant \( T \) (the capacity of the bath), the less the variation of caustic soda brought into. The smaller \( T \) the earlier the control reaction of the concentration in the bath.

4. Measurement of the Concentration of Acid Solution by pH and Its Control

In order to make such a control, the concentration of acid solution in the neutralization bath must be measured. There is a method of directly measuring the concentration, for example, electric conductivity in the solution. But in the solution are there floating particulates, such as fibrils. This causes an error of measurement. So this method cannot be recommended as a best one.

For this reason, we tries to devise an automatic titration method, without measuring directly the concentration, to make the value of pH constant by titrating the sampled acid solution by a caustic solution.

In this method, some amount of acid solution in the neutralization bath is taken out into a small reactor by a plunger pump as illustrated in Fig. 6. A designated amount of caustic soda (neutralization solution) which is beforehand prepared is supplied into the small reactor to give rise to a neutralization reaction there. The concentration of caustic soda solution into the neutralization solution shall be so set as to make the desired concentration of the acid solution just enough to neutralize. Then the value of pH in the small reactor is measured. If the concentration in the neutralization bath is a desired concentration, it will indicate pH 7. However, since the fabric always leaves the caustic soda behind and carries acid with it, the acid concentration in the neutralization bath grows dilute, say pH > 7. On the other hand, the output force of pH controller opens the valve and fresh acid solution is supplied to keep always pH 7.

Generally there is such a relation between pH value and the solution concentration as Fig. 7. Namely the value of pH varies greatly around pH 7 with a variation of acid or alkali concentration. This means that the value of pH has an on-off characteristics to the concentration of the solution. Therefore, as far as the value of pH is considered as a control output force, the operation must have the on-off characteristics. However, from the above consideration, the on-off controller will do enough to control the concentration in the neutralization bath.

In this controlling by pH value, all setting values are pH 7 for any concentration in the neutralization baths. So only varying the setting of concentration or plunging amount, alkaline solution control of more than two neutralization baths are possible by a sampling pH controller. Accordingly, this method is advantageous from the fact that the control against the two or more baths is made cheaply.

For actual example, the results of the control of the neutralization bath during the mercerizing process is shown. The constants needed are:

- \( C_i = 0.5 \) [N]
- \( C_x = 0.1 \) [N]
- \( V = 600 \) [l]
- \( v = 80 \) [m/min]
- \( q_s = 0.11 \) [l/m]
- \( w_s = 3.0 \) [l/min]
- \( P = 0.09 \) [l/m]
- \( C_sN = 1.0 \) [N]

\( \alpha \) is assumed to be 1 because the fabric is staying long enough in the neutralization bath. Then the constant value of the process: \( T = 66.7 \) [min] is obtained from eq. (16).

From the above numeric values, the eq. (15) becomes

\[
\Delta C(S) = \frac{0.04}{66.7S+1} - \frac{0.78}{66.7S+1} \Delta C_x(S)
\]
The result of this control is shown in Fig. 8, which shows it is reaching a desired value.

5. Conclusions

For the purpose of controlling the acid solution concentration in the neutralization bath, we theoretically analyzed the behavior of neutralization process and tried to apply our automatic titration method to actual processing with the following results:

1) The neutralization process can be theoretically analyzed by a mass transfer equation.
2) This analytical results give important suggestions of the design of the neutralization process and the control of the concentration of the neutralization bath.
3) The dynamic characteristics of the neutralization bath are first order shown by eq. (15).
4) As a controller of the concentration of acid solution in the neutralization bath, the on-off controller will do enough judging from the analytical results.
5) As far as the on-off controller is employed, for the measurement of acid solution concentration the pH values by the titration can be used.
6) The feed back control method by the titration is in details shown and could be applied to the neutralization bath of actual mercerizing process.

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