ADCHEM 2006

International Symposium on Advanced Control of Chemical Processes
Gramado, Brazil – April 2-5, 2006

CONTROL ORIENTATED B-SPLINE MODELLING OF A DYNAMIC MWD SYSTEM

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Abstract: A detailed dynamic model has been developed for the molecular weight distribution (MWD) of styrene bulk polymerization in a continuous stirred tank reactor (CSTR). The moment techniques are applied to formulate the MWD parameters based on the Schultz-Zimm distribution. In order to provide a general model for MWD control, the B-spline approximation has been introduced into the dynamic MWD modelling and the scanning least-square algorithm has been used for parameter estimation of the B-spline weights model. Under simulation environment, this model has been proved to be efficient for feedback MWD control.

Keywords: Molecular weight distribution (MWD), Dynamic model, B-spline approximation, Probability density function (PDF) control

1. INTRODUCTION

The B-spline neural network has been considered as an efficient tool for modelling the output probability density function (PDF) because it provides a general form in describing arbitrary continuous functions. Using the B-spline approximation, the output PDF will be described by the weights of the pre-specified basis functions. Dynamic characteristics of the weights vector can be developed from the data pairs of control input and output PDF so as to formulate the B-spline model for PDF control. In most of the previous works on output PDF modelling and control, it is normally assumed that the weights dynamics are known or the weights vector is available for the PDF approximation. This is partly because some of those works are concentrated on PDF controller design rather than B-spline modelling. It is also because that the B-spline modelling process itself is quite challenging considering the complexity of a dynamic PDF system. Many technical details have to be addressed carefully in order to guarantee the modelling efficiency. A scanning identification algorithm has been developed for the B-spline PDF modelling (Wang, 2000), however, it has been used mainly for static PDF systems or linear dynamic weights systems (Wang and Wang, 1998; Zhang and Yue, 2004). No work has been reported on B-spline modelling using the input and output PDF data from a nonlinear dynamic process so far. This motivates the endeavor of the work in this paper.

A molecular weight distribution (MWD) system has been taken as the case for study. The PDF data used for B-spline modelling are produced from the first-principle MWD model. Although the theory of B-splines is well-developed in approximation theory and linear control (Zhang *et al.*, 1997; Sun *et al.*, 2000; Kano *et al.*, 2003), to our knowledge, no applications to MWD systems have been reported except for a few works by

[1] Partially supported by the Outstanding Overseas Chinese Scholars Fund of Chinese Academy of Sciences (2004-1-4)

the authors (Yue *et al.*, 2004; Wang *et al.*, 2005). The MWD calculation in the previous works is not based on real dynamic models, only the static solution at different situations are considered. In this paper, the MWD model is developed from the polymerization reaction mechanisms with dynamic behaviors. Although the first-principle MWD model can be described by the well-known Schultz-Zimm distribution for this example, the model is further developed by B-splines. This is simply because a general-form MWD model is expected for the purpose of MWD control using PDF control strategies.

Notations

I initiator or its concentration $(mol \cdot L^{-1})$
I^{00} initial initiator concentration $(mol \cdot L^{-1})$
I^{0} controlled initial initiator concentration $(mol \cdot L^{-1})$
K_d initiator decomposition rate constant (min^{-1})
K_i initiation rate constant $(L \cdot mol^{-1} \cdot min^{-1})$
K_p propagation rate constant $(L \cdot mol^{-1} \cdot min^{-1})$
K_{trm} chain transfer rate constant $(L \cdot mol^{-1} \cdot min^{-1})$
K_t termination rate constant $(L \cdot mol^{-1} \cdot min^{-1})$
M monomer or its concentration $(mol \cdot L^{-1})$
M^{00} initial monomer concentration $(mol \cdot L^{-1})$
M^{0} controlled initial monomer concentration $(mol \cdot L^{-1})$
R_j live polymer of chain length j or its concentration $(mol \cdot L^{-1})$
R total concentration of live polymer radicals $(mol \cdot L^{-1})$
P_j dead polymer of chain length j or its concentration $(mol \cdot L^{-1})$
P total concentration of dead polymer $(mol \cdot L^{-1})$
T reaction temperature (K)
F total feed flow rate $(L \cdot min^{-1})$
V volume of reaction mixture (L)
θ average residential time (min)

2. POLYMERIZATION PROCESS

The process of interest is a styrene bulk polymerization reaction in a continuous stirred tank reactor (CSTR), in which styrene is the monomer for polymerization and azobisisobutyronitrile is used as the initiator. These two flows are injected into the CSTR with the input ratio defined as

$$c = \frac{F_M}{F_I + F_M} \tag{1}$$

where F_M is the flow of monomer and F_I is the flow of initiator. By changing c, the initial concentrations of the two main reaction species will be changed, which will change the output molecular weight distribution. To simplify the process, the reaction temperature is assumed to be kept constant during the control process.

The following free radical polymerization mechanisms are considered for the system.

- Initiation
  $I \xrightarrow{K_d} 2R^*$
  $R^* + M \xrightarrow{K_i} R_1$
- Chain propagation
  $R_j + M \xrightarrow{K_p} R_{j+1}$
- Chain transfer to monomer
  $R_j + M \xrightarrow{K_{trm}} P_j + R_1$
- Termination by combination
  $R_j + R_i \xrightarrow{K_t} P_{j+i}$

Accordingly, the mass balance equations are derived to be

$$\frac{dI}{dt} = (I^0 - I)/\theta - K_d I \tag{2}$$

$$\frac{dM}{dt} = (M^0 - M)/\theta - 2K_i I - (K_p + K_{trm})MR \tag{3}$$

$$\frac{dR_1}{dt} = -R_1/\theta + 2K_i I - K_p M R_1 + K_{trm} M(R - R_1) - K_t R_1 R \tag{4}$$

$$\frac{dR_j}{dt} = -R_j/\theta - K_p M(R_j - R_{j-1}) - K_{trm} M R_j - K_t R_j R \ (j \geq 2) \tag{5}$$

$$\frac{dP_2}{dt} = K_{trm} R_2 M + K_t R_1^2 - P_2/\theta \tag{6}$$

$$\frac{dP_j}{dt} = K_{trm} R_j M + \frac{K_t}{2} \sum_{l=1}^{j-1} R_l R_{j-l} - P_j/\theta \quad (j \geq 3) \tag{7}$$

where $\theta = V/F$ is the average residential time of the reactants in the CSTR. Denote

$$R = \sum_{j=1}^{\infty} R_j \tag{8}$$

$$P = \sum_{j=2}^{\infty} P_j \tag{9}$$

as the total concentrations of radicals and polymers, respectively, the following formulations can be established from (4) to (7)

$$\frac{dR}{dt} = -R/\theta + 2K_i I - K_t R^2 \tag{10}$$

$$\frac{dP}{dt} = -P/\theta + K_{trm} M(R - R_1) + \frac{K_t}{2} R^2 \tag{11}$$

R_1 in (11) can be ignored compared with R due to its low concentration, i.e.,

$$\frac{dP}{dt} = -P/\theta + K_{trm} M R + \frac{K_t}{2} R^2 \tag{12}$$

3. FIRST-PRINCIPLE MWD MODEL

3.1 Static MWD Model

The static solution to the concentrations of the reaction species can be derived from their dynamic equations. Denote

$$\alpha = 1 + \frac{K_{trm}}{K_p} + \frac{K_t R}{K_p M} + \frac{1}{K_p M \theta} \tag{13}$$

By taking the differential equations(2),(3), (10) and (12) to be zero, there are

$$I = \frac{I^0}{1 + K_d \theta} \tag{14}$$

$$R = \frac{-1/\theta + \sqrt{1/\theta^2 + 8 K_t K_i I}}{2 K_t} \tag{15}$$

$$M = \frac{M^0}{1 + (K_p + K_{trm}) R \theta} \tag{16}$$

$$P = \theta (K_{trm} M R + \frac{K_t}{2} R^2) \tag{17}$$

Similarly, from equations (4)-(7), the static concentrations of radicals and polymers are

$$R_1 = \frac{2 K_i I + K_{trm} M R}{K_p M \alpha} \tag{18}$$

$$R_j = \alpha^{-1} R_{j-1} = \alpha^{-(j-1)} R_1, \ (j \geq 2) \tag{19}$$

$$P_2 = \theta \left(K_{trm} M R_2 + K_t R_1^2 \right) \tag{20}$$

$$P_j = \theta \left(K_{trm} M R_j + \frac{K_t}{2} \sum_{l=1}^{j-1} R_l R_{j-l} \right), \quad (j \geq 3) \tag{21}$$

Substituting (19) into (20) - (21), and dividing (20) and (21) by the total concentration P, the normalized MWD at static state can be obtained to be

$$P_2 = \frac{\theta}{P} (\alpha^{-1} K_{trm} M R_1 + K_t R_1^2) \tag{22}$$

$$P_j = \frac{\theta}{P} \left(\alpha^{-(j-1)} K_{trm} M R_1 + \frac{j-1}{2} \alpha^{-(j-2)} K_t R_1^2 \right), (j \geq 3) \tag{23}$$

It can be seen that $\sum_{j=2}^{\infty} P_j = 1$. Therefore, the static MWD can be taken as a discrete probability density function of the chain length.

3.2 Dynamic MWD Model

For the dynamic MWD model, the distribution of P_j is not only a function of the chain length, but also a function of time. In this work, the moment method is introduced to setup the dynamic MWD description.

The moments of the number chain-length distributions of radicals and polymers are defined as

$$U_k = \sum_{j=1}^{+\infty} j^k R_j, \ \ k = 0, 1, 2, \cdots \tag{24}$$

$$Z_k = \sum_{j=2}^{+\infty} j^k P_j, \ \ k = 0, 1, 2, \cdots \tag{25}$$

It can be seen from (8) and (9) that $U_0 = R$ and $Z_0 = P$. Using the generation function technique, the differential equations of the leading moments for radicals are derived to be

$$\frac{dU_0}{dt} = -U_0/\theta + 2 K_i I - K_t U_0^2 \tag{26}$$

$$\frac{dU_1}{dt} = -U_1/\theta + 2 K_i I + K_p U_0 M - K_t U_0 U_1 + K_{trm} M (U_0 - U_1) \tag{27}$$

$$\frac{dU_2}{dt} = -U_2/\theta + 2 K_i I + K_p M (2 U_1 + U_0) - K_t U_0 U_2 + K_{trm} M (U_0 - U_2) \tag{28}$$

Similarly, the three leading moments of polymers are derived to be

$$\frac{dZ_0}{dt} = -Z_0/\theta + K_{trm} M U_0 + \frac{K_t}{2} U_0^2 \tag{29}$$

$$\frac{dZ_1}{dt} = -Z_1/\theta + K_{trm} M U_1 + K_t U_0 U_1 \tag{30}$$

$$\frac{dZ_2}{dt} = -Z_2/\theta + K_{trm} M U_2 + K_t U_0 U_2 + K_t U_1^2 \tag{31}$$

The mean and variance of the MWD are linked to the moments by

$$\mu = \frac{\sum_{j=2}^{+\infty} j P_j}{\sum_{j=2}^{+\infty} P_j} = \frac{Z_1}{Z_0} \tag{32}$$

$$\sigma^2 = \frac{\sum_{j=2}^{+\infty} (j-\mu)^2 P_j}{\sum_{j=2}^{+\infty} P_j} = \frac{Z_2}{Z_0} - \frac{Z_1^2}{Z_0^2} \tag{33}$$

Theoretically, an exact formulation of a molecular weight distribution requires countless number of moments, which is infeasible because of the computational load. An alternative method is to choose an appropriate distribution function to approximate the real MWD. For the polymer discussed in this work, the well-known Schultz-Zimm distribution is selected to describe the molecular weight distribution. It makes a simple analytical expression available for the scattering from the distribution. The normalized Schultz-Zimm distribution is defined by (Angerman, 1998)

$$f(n) = \frac{h^h n^{h-1} exp(-hn/M_n)}{M_n^h \Gamma(h)}, \ (n \geq 0) \tag{34}$$

where n is the chain length, h is the parameter indicating the distribution breadth, Γ is the gamma

function, M_n is the number average chain length which is defined as $M_n = Z_1/Z_0$. When $h = 1$, the Schultz-Zimm distribution reduces to the exponential Flory distribution, which is another commonly used distribution for MWD. The mean and variance of the Schultz-Zimm distribution are

$$\mu = \int_0^\infty nf(n)dn = M_n \tag{35}$$

$$\sigma^2 = \int_0^\infty (n-\mu)^2 f(n)dn = \frac{h+1}{h}M_n^2 - \mu^2 \tag{36}$$

By comparing (32), (33) with (35) and (36), the two parameters of the Schultz-Zimm distribution can be obtained to be

$$h = \frac{Z_1^2}{Z_0 Z_2 - Z_1^2} \tag{37}$$

$$M_n = Z_1/Z_0 \tag{38}$$

The calculation of the dynamic MWD can be divided into three steps:
(1) Get Z_0, Z_1, Z_2 from (2), (3), (26)-(31);
(2) Get h and M_n from (37) and (38);
(3) Formulate the MWD by (34).

4. DYNAMIC B-SPLINE APPROXIMATION

Although the dynamic MWD in this case can be described by the analytical Schultz-Zimm distribution function, it is not of a general form for the feedback PDF control scheme. Therefore, the B-spline approximation is introduced for the further model development. Consider a continuous PDF $\gamma(y, u_k)$ defined on $[a, b]$ interval, the linear B-spline neural networks can be used to approximate $\gamma(y, u_k)$ as:

$$\gamma(y, u_k) = \sum_{i=1}^{n} \omega_i(u_k) B_i(y) + e_0 \tag{39}$$

where u_k is the control input at sample time k; $B_i(y)(i = 1, \cdots, n)$ are the pre-specified basis functions defined on the interval $y \in [a, b]$; n is the number of the basis functions; $\omega_i(u_k)(i = 1, \cdots, n)$ are the expansion weighs; e_0 represents the approximation error which satisfies $|e| < \delta_1$ (δ_1 is a known small positive number). To simplify the expression, e_0 is neglected in the following. Denote

$$L(y) = \frac{B_n(y)}{\int_a^b B_n(y)dy} \tag{40}$$

$$c_i(y) = B_i(y) - L(y)\int_a^b B_i(y)dy, \quad i = 1, \cdots, n-1 \tag{41}$$

$$C(y) = [\, c_1(y), \quad c_2(y), \quad \cdots, \quad c_{n-1}(y)\,] \tag{42}$$

$$V_k = [\, \omega_1(u_k), \quad \omega_2(u_k), \quad \cdots, \omega_{n-1}(u_k)\,]^T \tag{43}$$

the static B-spline PDF model (39) can be represented in a compact form as

$$\gamma(y, u_k) = C(y)V_k + L(y) \tag{44}$$

Equation (44) is the static PDF model approximated by the B-spline neural networks, in which $C(y)$ and $L(y)$ are known when the basis functions are chosen. Denote

$$f_k(y) = \gamma(y, u_k) - L(y) \tag{45}$$

and consider the linear dynamics of the weights vector, the output PDF can be described by the following state-space B-spline model:

$$f_k(y) = C(y)V_k \tag{46}$$

$$V_{k+1} = EV_k + Fu_k \tag{47}$$

Here E and F are model parameter matrices. $f_k(y)$ can be further represented as

$$f_k(y) = C(y)(I - z^{-1}E)^{-1}(Fu_{k-1}) \tag{48}$$

and expanded to the following form according to matrix theory (Wang, 2000)

$$f_k(y) = \sum_{i=1}^{n-1} a_i f_{k-i}(y) + \sum_{j=0}^{n-2} C(y)D_j u_{k-1-j} \tag{49}$$

where

$$D_j = (d_{j,1}, \cdots, d_{j,n-1}) \tag{50}$$

By writing

$$\theta = (a_1, \cdots, a_{n-1}, D_0, \cdots, D_{n-2}) \tag{51}$$

$$\phi = (f_{k-1}(y), \cdots, f_{k-n+1}(y), C(y)u_{k-1}, \cdots, C(y)u_{k-n+1}) \tag{52}$$

Equation (49) can be written in the parameterized form of

$$f_k(y) = \theta\phi^T \tag{53}$$

Assume that the definition interval [a,b] can be discretized by a set of sampling points, the parameters a_i and $d_{j,i}$ can be estimated by the so-called scanning identification algorithm with the standard least-square update towards (53) (Wang, 2000). Figure 1 is provided to clarify the scanning process, in which y stands for the chain length varying from 2 to N, m is the total number of sampling points in terms of time.

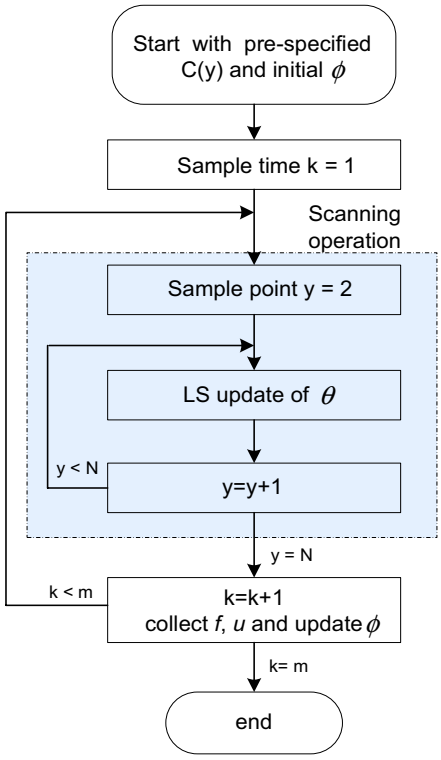

Fig. 1. scanning LS identification algorithm

5. MODEL VALIDATION

For the polymerization system in Section 2, firstly, the dynamic MWD data was produced from the first-principle model (fig. 2). The control input c was created randomly for the training purpose of the B-spline neural networks. Reaction system parameters are given in Table 1. In order to verify the formulation of the dynamic MWD, the steady-state solution of the dynamic model is compared with the results from the static MWD model. When $c = 0.5$, the MWD from the static model is given in fig. 3 and the steady-state MWD from the dynamic model is shown in fig. 4. The two curves are highly closed to each other, although the MWD in static model is an exact solution while the dynamic MWD is produced from the moments method, the generation function technique and finally represented by the Schultz-Zimm distribution. It shows that the moments method and the Schultz-Zimm distribution are appropriate for formulating this dynamic MWD model.

Secondly, the B-spline model was developed with the MWD data produced from the first-principle model. The scanning LS identification algorithm is used to obtain the parameter vector θ in (51). In this simulation, 10 fixed, 3rd-order B-splines are chosen for the MWD approximation. The training data length is 1500. The approximated MWDs with the trained B-spline weights are shown in fig. 5. It can be seen from fig. 5 and fig. 2 that the dynamic approximation is satisfactory.

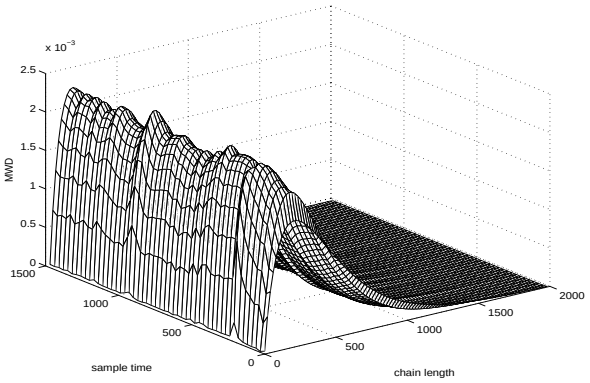

Fig. 2. Original MWDs from first-principle model

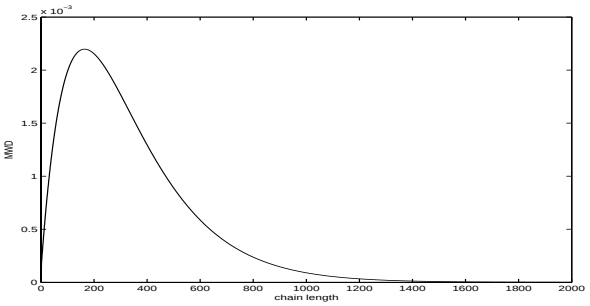

Fig. 3. Static MWD with c=0.5

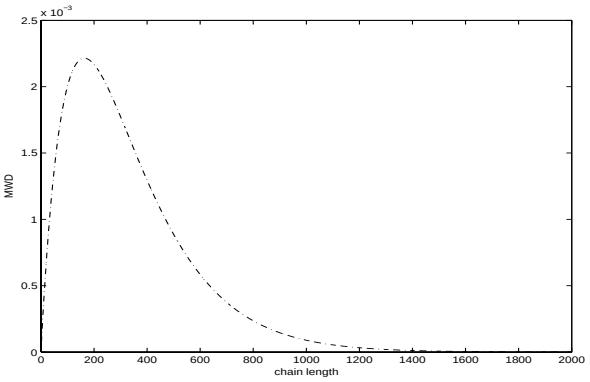

Fig. 4. Steady-state MWD with c=0.5

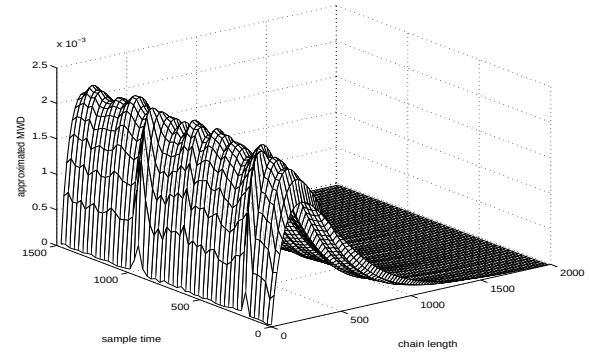

Fig. 5. Approximated MWDs from B-spline model

Table 1. Model parameters

K_d	$9.48 \times 10^{16} exp(-30798.5/rT)$
K_i	$0.6K_d$
K_p	$6.306 \times 10^{8} exp(-7067.8/rT)$
K_{trm}	$1.386 \times 10^{8} exp(-12671.1/rT)$
K_t	$3.765 \times 10^{10} exp(-1680/rT)$
V	3.927
F	0.0286
T	353
I^{00}	0.0106
M^{00}	4.81
r	1.987
c	[0.2,0.8]

Finally, the B-spline model was used for dynamic MWD control to see if the proper feedback control can be achieved with this model. The standard output PDF control is adopted with the following quadratic performance function (Wang, 2000).

$$J = \int_a^b (\gamma(y, u_k) - g(y))^2 dy + \frac{1}{2}\lambda u_k^2 \qquad (54)$$

where $g(y)$ is the target distribution and $\lambda > 0$ is a weighting factor for control energy. Fig. 6 shows the initial, final and target MWDs. Fig. 7 shows the development of output MWDs during the control process. Although there exists a small steady-state MWD tracking error, the controller successfully moves the output MWD from its initial shape towards the target shape. This means that the B-spline model can provide reliable MWD estimation for the feedback MWD control.

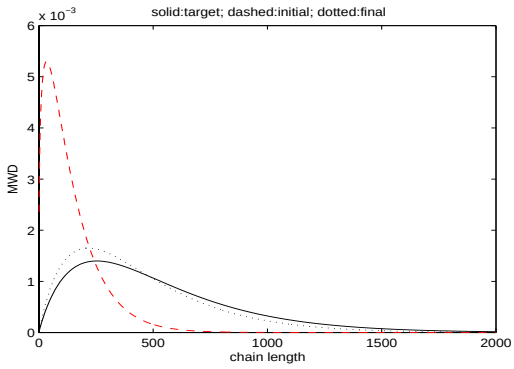

Fig. 6. Initial, final and target MWDs

6. CONCLUSIONS

In this paper, a dynamic first-principle MWD model has been developed and then approximated by the general B-spline functions. It makes the feedback MWD control feasible with the recently developed output PDF control strategies. Based on this model, further progresses on MWD control with different control strategies have been achieved and results will be distributed in the future.

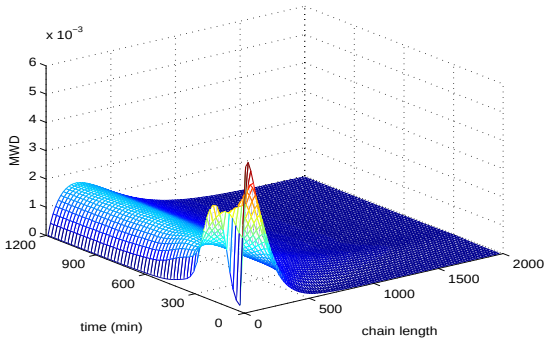

Fig. 7. Output MWDs during control

ACKNOWLEDGMENTS

The authors would like to thank J. Zhang and H. Wu for the help in developing BASIC and MATLAB programs.

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