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Research on the rheological properties of pesticide suspension concentrate

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Abstract: This study reports research on pesticide suspension rheology and a new rheological parameter, the relative value of approach, which has great advantage for judging the physical stability of a pesticide suspension concentrate. Experiments showed that the system can form stable dispersions when the value of the relative value of approach (S_r) is less than 0.1.

Key words: Suspension concentrate, Rheology, Stability, Relative value of approach
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INTRODUCTION

Pesticides formulated as suspension concentrate are better than many other pesticide preparations as they have advantages in terms of biological efficacy, safety, and economic viability (Kanellopulos, 1974; Mulqueen *et al*., 1990; Seaman, 1990; Wigger and Guckel, 1989; Zhang, 2002). Consequently this type of formulation has become widely accepted by agricultural users. However, the difficulty in controlling the physical stability of the S.C. is one of the major limitations to its development (Brian, 1980; Cheng, 1980; John, 1987; Makarov *et al*., 1988; Luckham, 1989; Guido and Tadros, 2000).

Rheology is a science which deals with material flow and deformation. The rheological properties of an S.C. pesticide formulation can be either Newtonian or non-Newtonian; both aqueous or non aqueous dispersions can be prepared (Tadros, 1980; Chen *et al*., 2002).

One of the purposes of the current study was to gain insight into the stability of the S.C. A method for judging the physical stability of S.C. is very important in preparation of suitable formulation for pesticide S.C. (Winzeler *et al*., 1980; Woldemar *et al*., 1984).

THEORY OF PLASTIC FLUID

The suspension concentrates studied in this work were mainly plastic fluids; the characteristics of plastic fluids will be discussed initially (Fig.1).

The plastic property of a dispersing system is thought to be produced by a three dimensional network structure of particles that comprise the S.C. The network structure must be destroyed for the system to flow. In a plastic material, the system starts to flow once the stress exceeds a fixed value. The more the shear stress increases, the more the structure is destroyed, and the viscosity will decline

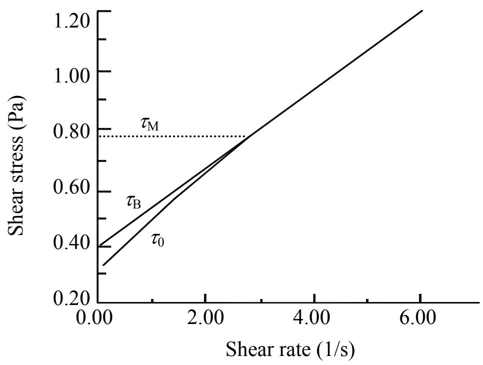

Fig.1 Rheological curve of plastic fluid

simultaneously.

Winzeler thought that the system has three yield values that are shown in Fig.1. τ_0 is static shearing force which Winzeler (1980) called it the value of plastic deformation. τ_B is called motive shearing force (or Bingham value) which is the value of the part of line extending to the ordinate. τ_M is the shear stress of the system starting to flow and corresponds to the shear stress of a single particle appearing in the flowing system when the particle structure of the whole system is destroyed. Here τ_0 is obtained from the Epprecht equation:

$$\tau_0 = \frac{2\tau_1\tau_2(D_2 - D_1)}{2(D_2\tau_2 - D_1\tau_1)} - \frac{\sqrt{[2\tau_1\tau_2(D_2 - D_1)]^2 - [2(D_2\tau_2 - D_1\tau_1)]^2(D_2\tau_1^2\tau_2 - D_1\tau_1\tau_2^2)}}{2(D_2\tau_2 - D_1\tau_1)} \tag{1}$$

For non-Bingham fluid, the equation is:

$$\tau = k_0 D^n + \tau_0 \tag{2}$$

RHEOLOGICAL MODEL

Creation of rheological model

In a Bingham fluid, the fluid starts to flow after the shear stress exceeds the yield stress τ_B. This phenomenon can be explained as follows: in a three-dimensional structure, the fluid at rest can resist a fixed shear stress and does not flow until the stress exceeds the Bingham yield value. The relative movement of particles in the interior of the system does not occur until the stress exceeds the value. If the weight of particles is not sufficiently large, the Brownian motion between the particles cannot reach the yield value. Thus, the system can only keep stability in a fixed scope.

The structure of a non-Bingham fluid is not as good as that of a Bingham fluid; because its Casson yield value is less than the Bingham yield value of Bingham fluid. Therefore, the particles cannot be arranged well when the system is at rest.

We can draw the conclusion that the more a system approaches the ideal state, the more stable it is. The parameter S_r is applied to judge the distinction between non-Bingham and Bingham fluid. The smaller S_r is, the more stable is the system. The equation of S_r is as follows:

$$S_r = \Delta S / S_B \tag{3}$$

The curves of *CE* and *BE* overlap from the point 'E'. ΔS is the area of BCE, which means the distinction between a non-Bingham and a Bingham fluid and its unit is Pa/s; S_B is the area of quadrilateral BOAE, and its unit is also Pa/s (Fig.2).

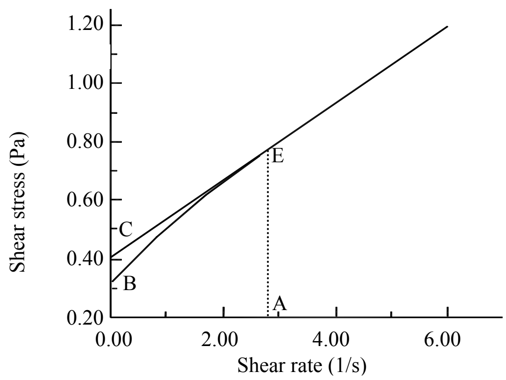

Fig.2 Legend of non-Bingham fluid and Bingham fluid

Verification of rheological model

The normal method of evaluating pesticide S.C. physical stability is to measure the suspending ratio after it is stored for two weeks at (54±2) °C. The higher the suspending ratio, the more stable is the S.C. When the suspending ratio is less than 90%, the S.C. will be unstable.

To investigate the S.C. rheology, we developed 30% thiram-triadimefon S.C. After studying the formulation, we found that dispersants, viscosity regulators and wettable agents were the major factors influencing the S.C. stability. First, the 10 samples (W-01~W-10) were obtained by orthogonal experiments. Then, we measured their values of S_r and suspending ratios (Table 1).

As can be seen from Table 1, the S.C. was stable only when S_r was less than 0.1. The more the value of S_r approaches zero, the more stable S.C. is. On the other hand, the higher the value of S_r, the bigger is the deviation from Bingham fluid behavior, and the more unstable is the S.C.

APPLICATION OF THE RHEOLOGICAL MODEL

The rheological model was applied to measure the physical stability of 40% chlorothalonil S.C. supplied by Suli Fine Chemistry Co., Ltd. (Jiangyin, China).

Measurement of viscosity

The viscosity values of 40% chlorothalonil S.C. were measured at (30±1) °C by using NDJ-79 Rotary Viscometer (Table 2).

Determining the curve type

Table 2 data were used to construct the curve of 40% chlorothalonil S.C. (Fig.3). Fig.3 shows that the system is a plastic fluid. Eq.(2) was used to obtain values of k_0, n and τ_0 as follows:

$$\tau - \tau_0 = k_0 D^n \Rightarrow$$
$$\log(\tau - \tau_0) = n\log(D) + \log(k_0) \Rightarrow$$
$$Y = BX + A$$

where, $B=n$; $A=\log(k_0)$; $Y=\log(\tau-\tau_0)$; $X=\log(D)$. In this way, we have changed the curve to a line. The theory of curve fitting was used to get the resulting equation corresponding to the equation ($Y=BX+A$) as:

$$\begin{bmatrix} \sum 1 & \sum x_i \\ \sum x_i & \sum x_i^2 \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum x_i y_i \end{bmatrix}$$

and we can get the values of A and B. Changing X and Y of the equation to τ and D will yield the equation of non-Bingham fluid (Fig.4) as

$$\tau=0.52D^{0.43}+0.16$$

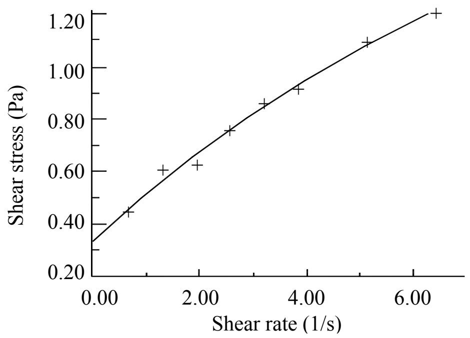

Fig.3 The flow curve of the system

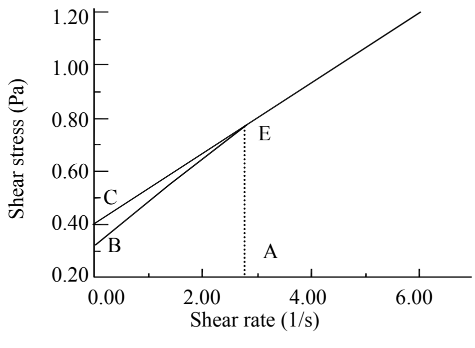

Fig.4 Curve of non-Bingham fluid

Table 1 S_r and suspending ratio of W-01~W-10

Exp.	W-01	W-02	W-03	W-04	W-05	W-06	W-07	W-08	W-09	W-10
S_r	0.079	0.146	0.082	0.147	0.093	0.064	0.187	0.070	0.024	0.020
Suspending ratio (%)	92.4	88.7	91.2	84.5	90.3	95.0	82.1	93.5	97.2	98.3

Table 2 Shear stress and shear rate of 40% chlorothalonil S.C.

D (1/s)	0.6283	1.2566	1.8849	2.5132	3.1416	3.7698	5.0264	6.2832
η (cp)	700	472	328	299	270	241	215.5	190
τ (Pa)	0.4398	0.5969	0.6182	0.7514	0.8482	0.9085	1.0832	1.1938

Estimation of D_E and τ_E

According to the above theory of plastic fluid, the system starts to flow once the stress exceeds a fixed value. When $\log(\eta_1-\eta_2) \leq 10^{-9}$, we can get

$$D_E=3.90107, \quad \tau_E=1.19496$$

Solving the equation of Bingham fluid

We constructed the curve of non-Bingham fluid using Graf4win and got the relevant equation by line regress. The equation of Bingham fluid is

$$\tau=0.74+0.09D$$

Getting the value of the relative value of approach (S_r)

From Fig.4 and the equations of non-Bingham fluid, and Bingham fluid, we can obtain the value of the area of *BCE* as

$$\Delta S = \int_0^{3.90107} [(0.74+0.09x)-(0.52x^{0.43}+0.16)]\mathrm{d}x = 0.223,$$

the area of quadrilateral *AEBO* as

$$S_B = \int_0^{3.90107} (0.74+0.09x)\mathrm{d}x = 2.778,$$

and the value of relative approach (S_r) as

$$S_r=\Delta S/S_B=0.08.$$

The thiram-triadimefon S.C. system can form stable dispersion when the relative value of approach (S_r) is less than 0.1. The system should be stable when S_r of 40% chlorothalonil S.C. is 0.08. This experiment showed that the rheological parameter can be used to evaluate and foresee the physical stability of pesticide S.C.

CONCLUSION

The authors' S.C. rheology research is presented and a new rheological model, relative value of approach, is advanced to judge the physical stability of a pesticide S.C. by a quantitative method. The authors learned from the experiments that the system can form stable S.C. when the relative value of approach is less than 0.1. The experiments also showed that the results determined by the method of relative value of approach to evaluate and forecast the physical stability of S.C. is the same as that of the present storage method for two weeks at (54±2) °C. The former who needs only one day to judge the physical stability of S.C. can replace the latter. What is more, this method can evaluate and forecast the physical stability of pesticide S.C., which will benefit development of pesticide S.C.

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