PHYSICO-CHEMICAL PROPERTIES OF CHLOROPICRIN WITH VARIOUS SURFACTANTS

Shad Nelson and Husein Ajwa
USDA-ARS, Water Management Research Laboratory, Fresno, CA

The phase-out of methyl bromide (MeBr) by the year 2005 has led to the development of new technologies for pre-plant soil fumigation. Application of alternative soil fumigants through drip irrigation lines (drip fumigation) has become a viable method for applying some of these volatile pesticides. Chloropicrin (trichloronitromethane) is one alternative fumigant to MeBr and has been shown to provide pest control under drip fumigation. To ensure adequate soil chemical distribution in drip systems, chloropicrin (Pic) must be combined with a surfactant. The objective of this study was to determine which surfactants currently on the market would be an adequate emulsifier for Pic during long-term storage by evaluating chemical-surfactant stability, corrosivity, and fluidity. Furthermore, a static system was used to determine the difference of air-water distribution coefficients (Henry's constant [K_H])of Pic in the presence of a surfactant to the K_H of Pic without an emulsifier.

MATERIALS AND METHODS

This study evaluated in total 27 possible emulsifiers (EM) for Pic (Table 1). The long-term (6 – 10 months) stability of Pic in the presence to different emulsifiers was evaluated by visual observation. A total of 5-mL of a solution containing 95% Pic and 5% EM, and 1000 ppm of this solution in 5-mL of deionized water (DIW), was placed in 10-mL clear glass headspace vials, and crimp sealed with Teflon coated butyl rubber septa and aluminum seals. Triplicate samples were shaken on a reciprocating shaker for 1 h to ensure uniform distribution of Pic-EM mixture. Separation of the Pic-EM mix in pure solution or water was noted for those treatments with poor chemical-surfactant uniformity over time. All vials for every treatment were stored in the dark at 25 °C. The viscosity (fluidity) and color changes of each Pic-EM mixture were evaluated visually after d, weeks, and months over the 6 – 10 month storage period. Corrosivity tests of the Pic-surfactant mixtures on metal were prepare by placing a 2.5-cm penny nail into 5-mL of the 95% Pic/5% EM solution and sealed as stated previously over a 6 month period. The corrosiveness of each treatment was ranked according to a visual rating scale where 0 = no corrosion, 1 = very low and 10 = extremely corrosive. Changes in the liquid fluidity and color of each treatment were also evaluated throughout the course of the study. Air-water distribution coefficients (Henry's constants) were determined for Pic solutions with and without surfactants. Triplicate samples containing 35 mL of DIW was placed into 120-µL amber glass bottles. The bottles were crimp sealed, and 125 cc of headspace from each 10-mL 95% Pic/5% EM treatment vial was injected into its corresponding treatment bottle. The bottles were shaken for 1 h, and placed in the dark for 24 h to establish equilibrium of Pic in the air-water system. Ten µL of headspace was extracted from each bottle and injected into and analyzed using an Agilent 5973N mass selective detector (mass spectrometer). The K_H for each treatment was

determined by difference of total Pic concentration in 120-mL bottles without water to the air phase concentration of Pic in bottles with water.

RESULTS

The evaluations from this study showed that the Pic-surfactant mixture was unstable for several of the treatments resulting in chemical settling, floating, and non-uniform storage distribution in several surfactants (Table 1). The color of the majority of mixtures changed from an initial light yellow color to shades of dark yellow, orange, red, rust, brown and black. The fluidity of several treatments also changed into slightly viscous to gelled solutions after extended storage. This could result in the plugging of drip application equipment or drip emitters during the drip fumigation process. The corrosiveness of these treatments was observed to be greater in treatments where there was lower Pic-emulsifier stability than more stable mixtures. The Henry's constants for 12 of the 27 pesticide-surfactant mixtures were significantly different and usually higher than the air-water distribution coefficient for Pic alone (Table 2). These findings will be useful information for predicting chemical behavior under drip fumigation practices, so that elevated or excessive volatility of Pic can be prevented and to preserve adequate Pic concentrations within the rooting zone for good pest control.

Table 1. Visual discription of Pic with 5% emulsifier (EM) physical properties after six months incubation at 25 °C. Solution colors were initially light yellow, except Trt # 1 was bright red.

Trt #	Name of emulsifier	EM settles	EM stable	Uniform fluidity	Corrosive rating	Final color
0	Pic alone	no	yes	fluid	5	l. yellow
1	Trinity TS 101 + dye	no	yes	viscous	5	black
2	Uniqema Atlox	no	yes	gelled	4	rust
3	Stephan	no	yes	gelled	6	rust
4	Triton X-180	no	yes	viscous	7	red
5	Nanso EVM 50/NS	yes	no	fluid	8	red
6	Nanso EVM 62/N	yes	no	fluid	7	l. red
7	Neodol (R) 1-7	no	yes	viscous	4	yellow
8	Neodol (R) 1-5 32726	yes	no	viscous	4	d.yellow
9	Triton X-165	no	yes	viscous	10	orange
10	Tergitol XD	no	yes	viscous	1	orange
11	Capricorn 650DF	no	yes	fluid	6	orange
12	Chemtex 2245	yes	no	fluid	8	black
13	Chemtex A105	yes	yes	fluid	10	brown
14	Makon TD-18	no	yes	viscous	4	d.yellow
15	Makon DA-6	no	yes	fluid	4	d.yellow
16	Capricorn 700C	no	yes	viscous	9	orange
17	Toximul 3406F	no	yes	viscous	6	red
18	Makon TD-6	yes	no	viscous	5	d.yellow
19	Makon DA-4	no	yes	viscous	5	orange
20	Makon DA-9	no	yes	viscous	5	orange
21	Toximul 3406F	yes	no	gelled	6	rust
22	Toximul 3404F	yes	no	fluid	7	rust
23	Makon TD-12	no	yes	viscous	3	d.yellow
24	Makon TD-3	yes	no	fluid	5	d.yellow
25	Toximul 3403F	no	yes	viscous	5	rust
26	Atlox 4851B	no	yes	viscous	6	orange
27	Stepan Toximul 3473F	no	yes	viscous	5	orange

Table 2. Visual description of Pic with 5% emulsifier (EM) physical properties after six months incubation at 25 °C. Solution colors were initially light yellow, except Trt # 1 was red.

Trt #	Name of emulsifier	Henry's constant	K_H S. E.	Corrosive rating
0	Pic alone	0.087	0.008	5
5	Nanso EVM 50/NS	0.793	0.111	8
6	Nanso EVM 62/N	0.504	0.090	7
7	Neodol (R) 1-7	0.412	0.060	4
9	Triton X-165	-0.683	0.023	10
10	Tergitol XD	0.217	0.034	1
12	Chemtex 2245	0.577	0.089	8
13	Chemtex A105	0.244	0.029	10
20	Makon DA-9	0.792	0.198	5
23	Makon TD-12	0.293	0.016	3
24	Makon TD-3	0.436	0.034	5
25	Toximul 3403F	0.266	0.026	5
27	Stepan Toximul 3473F	0.319	0.154	5