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A Rapid Sulfuryl Flouride Dosing Device: A Case Study for Fumigation of Freight Containers

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Abstract—**Sulfuryl Flouride (SF) effectively destroys insects, fungi or bacteria that cause human disease and can spoil transported goods. We have found in year 2015 that many containers and the contents do retain harmful concentrations of SF, representing a significant health risk for warehousemen, store employees and consumers. We also have found that there was no accurate dosage control device using SF to fumigate import freight containers (IFCs) in the Port. The purpose of this study is to develop a rapid fumigation device which is based on modern electronic technology and the characteristics of SF. The device, if it meets the design parameters, should improve the efficiency of the fumigating procedure while achieving a satisfactory insecticidal action. It should also leave behind less pesticide residue and reduce environmental pollution and worker-related poisoning. The proposed device will consist of three components, one storage container called SF storage bottle, one control platform and one radiator. The device should be able to apply 660 g of gaseous SF in 70 seconds, and the dosage error to within ±5 g. The application validated that the device would function as intended, assuming proper usage and no defects in operation. The experimental results showed the device with the advantage of high accuracy on controlling the fumigant dosage, and high efficiency on improving the fumigation procedure.**

***Index Terms*—Sulfuryl Flouride, Dosage control, Application Device, Import freight containers.**

I. INTRODUCTION

At present, the Sulfuryl Flouride (SF) has been widely used in food industry around the world for pest control since this SF-based product is able to effectively kill various kinds of insects and rodents, regardless of the life stage during which the target pests are exposed to the pesticide [1]. The first major investigation on fumigant contamination in import freight containers (IFCs) was presented by Knol-de Vos [2] Rotterdam, the Netherlands. From 2006 to 2009, Alexandra et al. [3] have detected on fumigants in the air of more than 4000 IFCs units arriving in Hamburg and Rotterdam. They found in 2008 that every sixth container and its contents do retain harmful concentrations of various fumigants and chemicals. The level of residual toxic agent constitutes an unacceptable risk to workers and consumers handling the fumigated commodity. Employees working with fumigants (e.g. in agriculture) have examined remarkably frequent neurological symptoms and respiratory complaints [2]-[10].

A majority of fumigation experiments conducted in commercial food-processing facilities focused on efficacy against insects and /or on insect population rebounds following the treatment [11], [12]. Efficacy against various insect pests often relates to the fumigant concentrations (C) multiplied by the duration time (T). Structures with minimum leakage losses required the least amount of fumigant to attain $C \times T$ values of biological significance [13]-[15]. The C taken to kill insects at a given T cannot be altered unless the temperature is raised. Hence, the C is determined by the fumigant dosage.

Many companies had developed different types of facility to detect SF in the past years. However, there were few companies or organizations focused on the rapid SF dosing device. Dow AgroSciences had developed a micro-fumigation Calculator (Fumiguide Calculator) [16]. The calculator takes a variety of fumigation factors (such as pest species, growing season, wind speed, relative humidity, temperature, fan ventilation, fumigation time, the volume fumigation, soil type, etc.) into consideration, the specialized calculator was designed to determine the dosage of pesticide. Dow AgroSciences also had developed professional fumigation computer software - SF Fumiguide, which not only performed the function as the calculator in the process of fumigation, but also controlled the fumigant dosage of SF in a timely manner according to the C inner the fumigation containers. [17] developed a system operated on a computer running Windows 95 and PCL812 combination card and a PCL740 digital-output card for precise fumigation of a silo with SF. The above fumigation systems are able to maintain an effective and stable fumigant C in the containers and are beneficial to the containers fumigation. But these systems lead to a heavy computational burden. They are not suitable to apply in Port where the IFCs are frequently delivered; especially those sites without power available.

IFCs must be disinfected and sterilize in the Port before they enters the inland in China. The process of disinfection and sterilization is the trailer tows the IFCs to a pre-specified site (the specified site will be changed in respects to the flow of cargo), and then the technical workers use a particular tool to inject gaseous SF into the IFCs. The whole process should be completed within 3 minutes include the trailer pass in and out the application sites. The process time would even be shortened in a busy time. Different corporate containers were often piled up in their specified district. They would be fumigated at a later time. The distances between the two rows of the containers were less than 1 meter. Hence, this sites requiring a flexible SF dosing device.

Before the first trailer entering the fumigation sites, the technical workers would have calculated the pesticide dosage according to the ambient temperature using fumigation calculation software. In general, a bottle of SF can be distributed into a total of 15 containers (660 g for each container). Traditionally, to complete the application task mainly depends on the experienced technicians operate the manual valve (MV) of the SF storage bottle (SFSB) working time. Due to the liquid SF (LSF) needs to absorbing a large number of heats when it converting into gaseous, after the SFSB was continually operated 6 times, the operator must place the SFSB in a horizontal position for next application. When the application got to more than 10 times, if without interruption at least half an hour in a 20℃ ambient temperature condition, the SFSB must be lay upside down for next application. For these reasons, the application needs two operators working together. After 4 hours that the technicians had fumigated the 300 units empty IFCs, we have tested the SF on *C*. We found that the applied SF dosage of all the IFCs which was fumigated by the first three applications from the SFSB were over more than 720 g and were less than 550 g in the last 3 applications. The actual need were 660±20 g. Obviously, most of the fumigation results were unacceptable. Therefore, constructing a rapid SF dosing device (RSFDD) based on an automatic and real-time control platform is an urgent need for fumigation.

Along with the rapid improvement of today's micro-fabrication technology and embedded systems, a tiny electronic sensor is able to integrate multiple functions, such as precise sensation and calculation [18]-[20]. By integrating the latest in sensory chips and micro fabrication technology with traditional vaporizer, modern sensor modules and solenoid valve (SV), an accurate RSFDD can be established, together with powerful processing ability. Therefore, the main purpose of this study is to construct an accurate RSFDD. It is desired that at the end of using this device the fumigant dosage of SF be significantly accurate and the process itself be environmentally safer than those process presently used in the Port. The specific objectives of the study are as follows:

(1). To develop the experimental data capture system which the hardware and software design are involved.
(2). To verify the method on site.

II. MATERIALS AND METHODS

The basic make-up of our system can be divided into three major parts: the SF storage bottle (SFSB), the vaporizer and the control platform (CP).

A. The SF, SFSB, and Modified SFSB

The characteristics of LSF are: boiling point is -55.2℃, Molecular Weight is 102.6, latent heat of vaporization is 233.5 KJ kg^{-1}, Liquid Specific Heat Volume is 1.4 KJ kg^{-1} k^{-1}, and density is 1.194 kg m^{-3}.

Figure 1a shows the outline of SFSB before it was modified. The MV is the only switch to control the flow of SF during application. SF was applied to the IFCs as a liquid under pressure, through introduction tubing, the liquid immediately converts to gas when released from the tubing, utilizing the heat in the surrounding. However, given the limited headspace within the storage facility, air movement, and ambient temperature within application site, a liquid SF of this nature is not optimal for achieving rapid equilibrium within the storage facility; this is the reason why we modify the structure of SFSB. The modified SFSB is shown in figure 1b. There is a PVC catheter with 20 mm o.d. and 10 mm i.d. stretching from the bottle-entrance to the place 10 mm above the bottom. The curve about pressure relative to the temperature of the internal SFSB applied in this study shows in figure 1c. From the chart we can see that the internal pressure will be raised rapidly follows the temperature increasingly. Hence, it is a dangerous operation to use extra heat producer to heat the SFSB during dosing process.

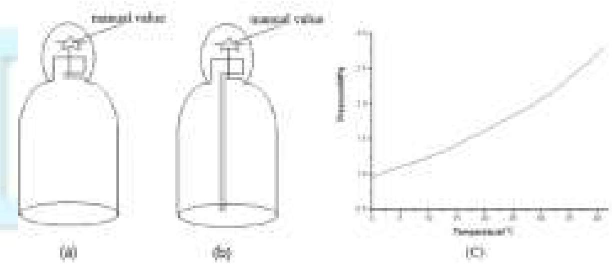

Figure 1. (a) SFSB before modification; (b) SFSB after modification; (c) characteristic curve about the pressure relative to the temperature inner the SFSB

B. The Vaporizer

Since the goods of the IFCs are unknown, therefore, the LSF cannot directly inject into the IFCs avoid the goods being damaged. So, we need a vaporizer to turn the LSF into gaseous. The vaporizer is a bent copper tube with heat sink; it makes the LSF internal the vaporizer easy to exchange heat with the surrounding. The heat exchanger area can be worked out according to the equation 1 to 3.

$Q_1 = cm(t_2 - t_1)$ (1)

$Q_2 = Lm$ (2)

$kA = Q_1 + Q_2 \quad k \in [200, 250]$ (3)

Where Q_1 [J] is the absorptive heat (from storage temperature t_1 [℃] to evaporation point t_2 [℃]) of LSF, and Q_2 [J] is the evaporation heat, c [KJ kg^{-1} ℃$^{-1}$] is the specific heat volume of LSF, m [kg] is the fluid quality, L [KJ kg^{-1}] is the latent heat of LSF, A [m^{-2}] is the heat exchanger area of vaporizer. Taking the availability factor of the vaporizer into account, the heat exchanger area was set as 2 m² in this work.

C. The Control Platform (CP)

The structure of the CP is described as follows: circuit was designed using the STC12C5A60S2 microcontroller as the central functional processor. It is a new generation of 8051 developed by STCMCU technology (Shenzhen, GuangDong, China) co., LTD. It is a single machine cycle (1T) microcontroller with high-speed, low power consumption, strong anti-interference and working frequency ranging from 0 to 35 MHz which is equivalent to the scope 0 to 420 MHz in an ordinary 8051. The Keil C51 (integrated development environment) applies to debug the software and generates Hex code, a STC Programmer use to download the Hex file into the microcontroller. This microcontroller serves to encode data packets and dispatch control commands among the modules used in the CP. In addition, the CP also includes an A/D convertor, a weighing sensor, a 6-digit-seven-segment-display, a solenoid valve, nine switches, an infrared receiving circuit, a remote control, and a storage battery. The inner pressure of the SFSB is quite high, and it leads the LSF with a high-speed to flow through the SV, thus the signal of the weighing sensor might be altered rapidly. Hence, the microprocessor should have enough data processing ability. Taking into the cost, at present, the STC12C5A60S2 microcontroller is the optimal one.

The ∑-△ based A/D convertor was applied for herein. The type is TM7709 (Titan micro electronics, Shenzhen, Guangdong, China). It is able to achieve 24-bit without missing code, the device also can accept low level signals directly from the sensor and generates a serial digital output. The chip's A/D data update rate is determined by its system clock. In this work, its system clock was set as 5 MHz, and then the data update rate is 10 Hz. The A/D convertor was connected to the microcontroller via an i^{2}c (INTER IC BUS) port.

The weighing sensor is a piezoelectric transducer. Its resolution ratio is 1/100000; accuracy of measuring is 1/30000; maximum load is 50 kg. The output voltage $\triangle U_o$ [V] can be calculated as the equation 4.

$\triangle U_o = SF$ (4)

Where S [V Pa^{-1}] is the transducer sensitivity and F [Pa] is the external force or weight on the weighing sensor. The weighing sensor was shielded by a steel panel with 300 mm width, 400 mm length and 60 mm height. The SFSB was placed on the steel panel during application. The weighing sensor was connected to the A/D convertor through 4 parallel wires i.e., the +5 V (positive digital power), 0 V (negative digital power), the other two are the differential signal output.

The SV used in this study is the type of 1020/2 made by the Jingtian Machinery Factory (Shenzhen, Guangdong, China). The pressure resistance of the SV is 40 bar, ambient temperature is -35℃ to 110℃, rated voltage is DC 12 V, rated power is 6 W, circulation caliber is 1.0 mm, switching time is 0.03 second. The circulation caliber of the SV was calculated by the following equations which were based on fluid dynamics science.

$q_m = upS$ (5)

$F = ma$ (6)

$u = at$ (7)

$F = PS$ (8)

$S = \pi R^2$ (9)

$pPS^2 t = mq_m$ (10)

Where q_m [kg s^{-1}] is quality flow of the LSF pass through the SV, u [m s^{-1}] is flow velocity, p[kg m^{-2}] is fluid density, S [m^{-2}] is the crosscut area of circulating caliber, F [Pa] is pressure force to SV, m [kg] is fluid quality goes through the SV , a [m s^{-2}] is fluid accelerated speed, t [s] is fluid via the SV time, P [kg m^{-2}] is intensity of pressure inner the SFSB, and R [m] is the radius of circulation caliber. The operation of the SV was controlled by a MOSFET which was connected to the microcontroller by a GPIO (General Purpose Input/Output). The device could not achieve the required control accuracy if the bore diameter of SV was selected too large. Vice versa, the application time would significantly be prolonged if the bore diameter was selected too small.

The 6-digit-seven-segment-display used in the present study (XinSimei XSMS3661AR10, Shenzhen, GuangDong, China), which power consumption is low. This component possesses a 74HC573 which is octal D-type transparent latches featuring separate D-type inputs for each latch and 3-state outputs for bus oriented applications. The 74HC473 took up to the whole 8 GPIOs of the port 2 on microcontroller.

The Storage Battery is a rechargeable sealed lead acid battery made by HuaWei (Shenzhen, GuangDong, China), the type is FM1270A and the capacity is 7.0 Ah. The storage battery services as a power supply for the device.

The PT 2272 (Princeton Technology Corp., Taiwan) is a remote control decoder paired with PT 2262 utilizing CMOS Technology were used to the infrared receiver and infrared remote control part. The PT 2262 was linked to the microcontroller by the 4 GPIOs.

The basic processes which determine the quality of the introduced device are microcontroller, A/D convertor, SV, and weighing sensor.

□.DEVICE INTEGRATION AND IMPLEMENTATION

The electronic control circuit of our device consisted of seven parts which includes keyboard, display, buzzer, SV, RS232 interface, infrared receive, battery and their associated discrete components, each performing specific tasks. All seven parts and their associated discrete components were mounted and electrically connected on a printed circuit board assembly (PCBA). Based on mechatronics technology, the PCBA was housed in a 32 cm long x 15 cm width x 16 cm height PVC plastic box - control cabinet (CC). The hardware supports keyboard input and nixie tube display. There are 9 buttons in the proposed device, and their functions are summarized in table 1.

Table 1. The function of the buttons.

Items	Button Name	Function
1	DMCT	Cooperation with the POWER button to fulfill the weighing coefficient calibration
2	ACK	Identity the current setting
3	UP	Data increase
4	DOWN	Data decrease
5	SETTIN G	Modify the default parameter
6	SMALL	Small size containers' start and pause application switch
7	LARGE	Large size containers' start and pause application switch
8	OTHER	Other size containers' start and pause application switch
9	POWER	Power on/off switch

There were 4 buttons on the remote control i.e., L, S, O and A. They functions were corresponding to the LARGE, SMALL, OTHER, and ACK respectively in Table. 1. During the application process, the microprocessor triggers or break off the SV as soon as it receives the activation command from the remote control or keyboard, and then the introduction tubing transfuse the SF into the IFCs. The weighing sensor generates signal to the A/D convertor whenever whether the weight of SFSB varied. The microprocessor shuts off the SV immediately when it detect the actual application dosage equals or over than the setting. Simultaneously, the buzzer generates alarm. Figure 3 shows the software flowchart of the fumigation device during the application.

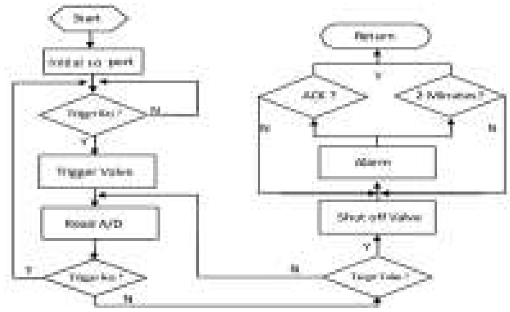

Figure 3. The application flowchart of the fumigation device

The weighing coefficient is important parameters for this device and it should allow to be calibrated since different weighting sensors with their properties, and the property would perhaps be changed with the application circumstance altered. In this work, the 5 Kg, 10 Kg, 20 Kg, 30 Kg and 50 Kg weights has been utilized to attain an appropriate weighing coefficient. The calibration procedure is (1) puts the counter poise on the weighing sensor; (2) manual inputs the actual weight of the counter poise to the microcontroller; (3) press "ACK" button after these two steps are completed. Then the microcontroller calculates the weighing coefficient and save the results in the RAM. The weighing coefficient assures us accurately measure the weight variation of SFSB.

Figure 4 shows the line diagram of the fumigation device and the prototype of the proposed device. The SV was served as a bridge between the SFSB and vaporizer.

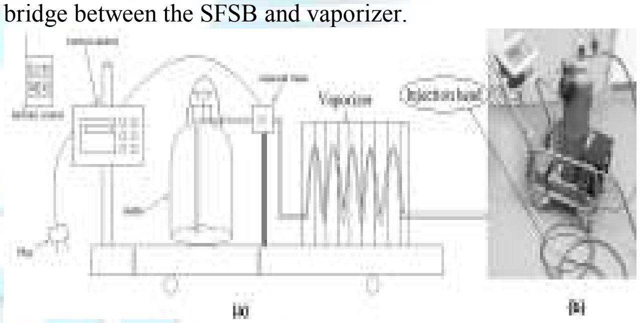

Figure 4. (a) Line diagram of the fumigation system and (b) the prototype of the proposed device

IV. EXPERIMENTAL RSULTS OF DEVICE PERFORMANCE EVALUATION

A. Testing Distance of the Remote Control

The approach for this testing is to confirm the remote controller whether suitable to the device. In an open field, the effective range is able to extend 10 m without any mistake. It is good enough for the proposed RSFDD. The RSFDD requires no special training for operation. The operator just needs to press the button of the remote control and the application would be executed automatically by the device. One operator can easily be completed the fumigation work.

B. Testing the LSF Change into Gaseous SF

The reason of this experiment was to analyze whether the LSF was entirely injected into the IFCs. A pail with 300 mm diameter and 500 mm height was filled with water was introduced to detect the gaseous SF output of the injection head (fig. 4b). After the SV being closed 7 seconds, the injection head was put into the pail, and we found that there were no continuous bubbles rising up. It should be noted that the heat transfer zone of the vaporizer should be large enough. Since the surface of the vaporizer would attract frost which was caused by LSF turns into gaseous state. The frost would influence the LSF turns into gaseous SF when the ambient temperature is lower than -10□ i.e. the vaporizer would hold a little fluid pesticide after it with apply in succession more than 7.

C. Testing the Device Dosing Accuracy

The purpose of this experiment was to determine the dosing accuracy of the device we designed. The experiment was done in empty container at a container yard on NingBo Port in May 2011. The weight of dosing counted by the RSFDD, and also estimated them with Fumiscope (Model 4.2, Key Chemical Equip., Clarwater, FL. USA) after the process has been completed 4 hours. The application dosage was set as 660 g. During test, the timer of the RSFDD and a Casio stopwatch (Model HS-80TW-1DF, Casio, Inc., Japan) were utilized to count the time. A digital thermometer with DS28EA00 (Maxim Integrated Products, Inc. Sunnyvale, USA) was used to detect the temperature. Table 2 summarize the averages testing result of 10 bottles without catheter, and Table 3 displays the averages testing result of 10 bottles with catheter. There was no record after application 8 times at the table 2. The reason was that the pressure of the SFSB was almost equal to the surrounding air which was caused by the temperature decreasing inside the SFSB. Hence, the SFSB was unable to push the SF flow out the storage bottle. Table 3 indicated that almost all the LSF was able to outflow from the storage bottle. The application time could be controlled within 80 seconds. The percent deviations of the application dosage were less than 1%. The Port required that the percentage deviations of the application dosage should be less than 3%. Due to the performance of the 24-bit A/D convertor, the dosage control could achieve to milligram, but a certain lead or lag control were inevitable to occur during the signal processing which would cause a ±5 g error fluctuates.

Table 2. the average testing result of 10 bottles without catheter (Ambient temperature：20℃).

Item	Application time (s)	Application dosage (g)	The interval time for the next application (s)	The surface temperature of the SFSB (℃)
1	23	667	60	20
2	24	665	60	10
3	37	659	50	2
4	40	661	60	-8
5	60	658	52	-15
6	82	660	50	-22
7	161	662	70	-30
8	813	655	60	-30

Table 3. the average testing result of 10 bottles with catheter (Ambient temperature：20℃).

Item	Application time (s)	Application dosage (g)	The interval time for the next application (s)	The surface temperature of the SFSB (℃)
1	60	664	56	20
2	60	663	60	20
3	60	663	48	20
4	61	664	60	20
5	61	659	52	20
6	63	662	50	18
7	63	663	70	18
8	63	662	50	18
9	63	660	60	18
10	65	658	50	18
11	65	662	42	16
12	65	660	40	16
13	70	660	45	16
14	70	661	50	16
15	70	661	70	16

The proposed device was providing a completed fumigation process in a shorter time and accurate dosing than has been possible heretofore in the Port. It relates generally to IFCs fumigation processes utilizing accurately control concentrations (dosage) of SF so as to be less hazardous during application and result in substantially less hazardous quantities of residue at the completion of the process, thereby reducing the weight of fumigant acquired by the process to be ultimately released into the atmosphere and reducing the environmental impact of the process as compared to those presently used.

D. The Realization Using Other Methods

We have developed a device to control the flow rate of the SF to employ in this fumigation. But due to the fact that the gas volume will vary with the temperature variation, even a temperature compensation algorithm was introduced in the software, the percentage deviations of the application dosage was still over than 5%. For this reason, the flow rate method based device is not suitable for this application.

We still have developed a device an additional 2000 W heat producer was encircled on the SFSB without catheter. Using temperature sensor to monitor the surface temperatures variation of the storage bottle, and an electronic circuit was used to control the heat producer ON-OFF time according to the temperature sensor information. This device was able to meet the requirement of the Port. Obviously, it is substantially an energy waste production and this device is not suitable for the sites where there is no power supply. Furthermore, potential risks of explosion still hide in the storage bottle if the temperature sensor would not work normally.

V. CONCLUSION

The proposed device was providing a completed fumigation process in a shorter time and accurate dosing than has been possible heretofore in the Port. It relates generally to IFCs fumigation processes utilizing accurately control concentrations (dosage) of SF so as to be less hazardous during application and result in substantially less hazardous quantities of residue at the completion of the process, thereby reducing the weight of fumigant acquired by the process to be ultimately released into the atmosphere and reducing the environmental impact of the process as compared to those presently used. The introduced device was flexible and it was suitable to the site where there was no power available and somewhere the car could not attained.

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