The necessity of using pure carbonyl sulfide to prevent corrosion on copper

Vermeidung von Korrosion an Kupfer durch den Einsatz von reinem Carbonylsulfid

YongLin Ren, Rudy Pratte and Jim Desmarchelier

Abstract

Fumigants need to be effective against insect pests but must not corrode or damage materials that they come into contact with. Carbonyl sulfide (COS), which is regarded as a potential alternative to methyl bromide, does not corrode copper when applied in a purified formulation. However, contamination of industrially manufactured carbonyl sulfide by hydrogen sulfide can cause corrosion on copper. Only pure COS should be applied for a fumigation.

Key words: Carbonyl sulfide, fumigation, stored products protection, materials protection, corrosion

Zusammenfassung

Begasungsmittel dürfen neben einer abtötenden Wirkung auf Schädlinge jedoch keine materialverändernden Eigenschaften aufweisen. Carbonylsulfid (COS), das als eine zukünftige Alternative zu Bromstilben im Vorratschutz angesehen wird, ist in seiner reinen Form nicht korrosiv. Geringe Verunreinigungen von Schwefelwasserstoff in industriell hergestelltem Carbonylsulfid wirken jedoch korrosiv auf Kupfer. Bei einer Begasung mit COS ist daher auf die Reinheit des Gases zu achten.

Stichwörter: Carbonylsulfid, Begasung, Vorratsschutz, Materialschutz, Korrosion
Introduction

The search for new fumigants to control pest infestations in stored products or in timber is motivated by the fact that certain fumigants will be phased out due to their destructive impact on the environment. Carbonyl sulfide (COS) is regarded as one of the potential alternative fumigants to those currently in use (Carter, 1993). The efficacy of COS against a variety of stored product insects has been studied in detail by Desmarcells (1994a, 1994b), Plarre and Reichmuth (1996, 1997), and Zettler et al. (1996, 1997). However, before a fumigant can be used to desinfect certain commodities or facilities, possible negative side-effects, like altering the properties of materials, must be ruled out. Most storage facilities are run by modern computer based technology, therefore, the application of any fumigant that might cause corrosion on copper will not be acceptable. Ren (1996) reported that COS was not degraded to hydrogen sulfide (H2S) and was also not absorbed by both copper tubing and copper powder at 75 % r.h. and 25°C. That is, in its pure form, COS does not corrode polished copper. However, contamination by as little as 1 ppm of elemental sulphur or H2S causes copper to discolor (Ferm, 1957), Plarre and Reichmuth (1997) found corrosion on copper during their trials and attributed the corrosive effect to H2S formed by degradation of COS to carbon dioxide (CO2) and H2S under the high relative humidity of 70 % ± 10 %. It is known that COS reacts in the presence of water or water vapor to form CO2 and H2S. However, because this reaction is very slow (Stock and Kuus, 1917; Ferm, 1957), and COS is relatively stable towards acids, with both H2S and CO2 being acidic, this is unlikely to have occurred in this case. It is more likely that the applied COS, with a purity of 97 %, was contaminated with small amounts of H2S prior to the fumigation. To investigate this belief, we conducted a corrosion study on copper using both unpurified and purified COS.

Materials and Methods

Two sections of polished copper pipes (25 mm x 5 mm o.d.) were placed in Erlenmeyer flasks (270 ml capacity) with ground-glass joints (Bibby Sterilin, Staffordshire, UK; Cat. No. FE 250/3). The atmosphere in the fumigation flasks before loading the pieces of copper and sealing of the flasks was conditioned at 70 ± 3 % relative humidity and 25 ± 1°C. The sealing tops with rubber septa were a cone screw thread adaptor (Quickfit, STS, Bibby Sterilin). Carbonyl sulfide (unpurified 100 mg/L or purified COS 100 mg/L) was injected with a gas syringe through a septum into the sealed flasks. An equivalent flask, which did not contain any samples was used as a standard flask to calculate the concentration of COS. A similar flask contained the copper samples but no COS, to provide an unfumigated copper standard. A sample of the gas in the headspace was injected into a gas chromatograph at timed intervals. The fumigated samples were compared to the unfumigated copper after 49 hours exposure and assessed for possible discoloration of the metal. The relative humidity in each of the flasks was measured at the end of the experiment by inserting a Vaisala HMI 41 humidity and temperature indicator, which fitted tightly in the opening of the flasks. Each treatment was duplicated.

The unpurified COS manufactured by Matheson Gas Prod. INC. (USA) was estimated to contain 86.1 % COS with the rest being H2S (10.4 %) and CO2 (3.5 %). In order to gain purified COS, the manufactured COS gas was bubbled through a cupric sulfate (CuSO4) solution to remove the H2S. It had an estimated purity of 96.5 % with 3.5 % of CO2.

The concentrations of COS were determined on a GOW-MAC mass density balance (GOW-MAC Instrument Co., Madison, NJ), after separation on a 1 m x 5 mm i.d. porapak Q 100/120 mash (Alltech Associates, Cat. No. 2702) at 105°C and carrier (N2) flow of 150 mL/min. The reference gas was tetrafluoroethane (> 99.9 % pure).

The gas concentration was checked daily by GC injection of a headspace sample of 20 μL. Carbonyl sulfide and H2S was determined on a GC-6AM Shimadzu GC (Shimadzu Seisakusho, Kyoto, Japan), fitted with a flame photometric detector (FPD), sulfur model. Separation was achieved on a 1 m x 3 mm i.d. glass column packed with HayeSep Q (Alltech Associates, Baulkham Hills, Australia, catalogue no. 2801) at 115°C and carrier flow (N2) of 40 mL/min at 0.8 psi.

Results

The relative humidity in the flasks at the end of the exposure was at 71 ± 4 %. The highest reading for the purified COS treatment was 73 % and 74 % for the unpurified COS treatment. Normally, fumigation is carried out at relative humidities of less than 70 %. Here a worst case scenario was tested because, for many commodities (such as wheat, barley, sorghum, paddy and maize), their moisture content is 13.5–14.5 % (wet basis) in equilibrium with a relative humidity of ~70.0 % at 25°C (Roberts, 1972).

The concentration of COS in the headspace over the copper tubing remained constant during the 49 hours exposure, as shown in Figure 1. That is, no loss of COS occurred in the headspace over the copper tubing compared with the control. This result indicates that COS was not degraded to H2S and was also not absorbed by copper tubing at 25°C and 71 % r.h. However, H2S was disappeared in the unpurified COS flask after 2 hours exposure. Based on this result, only H2S was absorbed by copper. These results are consistent with results from Ren 1996.

Tarnishing of copper tubing was assessed in blind tests by 12 people working in related areas but with no direct knowledge of, or input into this experiment. The results show that only the copper tubing, which had been exposed to unpurified COS, had a strong discoloration, a dark blue hue (Figure 2). The copper pieces exposed to purified COS showed very little change in colour compared to the unexposed control samples (Figure 2). Only 4/12 people identified a small amount of discoloration from purified COS, relative to the control samples. Based on these results, tarnishing of copper tubing was obtained from H2S. It is evident that COS was stable in the presence of copper at 25°C and 71 % r.h.

![Fig. 1. Concentration of carbonyl sulfide (COS) over the copper tubing (O), relative to COS in the absence of copper (Co).](image-url)
Untreated control

Treated with purified COS

Treated with unpurified COS

Discussion
In order to prevent corrosion it is very important to use only pure carbonyl sulfide. Even small amounts of H$_2$S contamination can cause noticeable changes in copper. Manufactured, ready to use COS has not the purity which is necessary to prevent corrosion effects. However, when purified COS is applied, corrosion will not occur, even at high humidities like 70%. The degradation of pure COS in high relative humidities is too slow to form corrosive H$_2$S.

Acknowledgments
The authors thank Dr. Jane Wright and Mr. Collin Waterford for fruitful advice and the Stored Grain Research Laboratory (SGRL) agreement for financial assistance.

Literature


Accepted: 2 February 2000

Author's address: Dr. Rudy Plarre. Bundesanstalt für Materialforschung und -prüfung, Lab. IV.11, Unter den Eichen 87, D-12205 Berlin

Nachrichtenbl. Deut. Pflanzenschutzd. 52. 2000

Fig. 2. Colour change of copper after treatment with carbonyl sulfide (COS) for 49 hours at 70 ± 3% r.h. and 25 ± 2°C.