NB: OPEN KNOW-HOW

Folpet and Captan Crop Protection Products.
The adverse impact of Perchloro Methyl Mercaptan.

ABSTRACT

This article examines the detrimental consequences of the presence of Perchloro Methyl Mercaptan (PCMM) as a contaminant in technical Folpet and Captan pesticides, focusing on its impact on the long-term stability of pesticide formulations. The author provides extensive assistance aimed at addressing quality and production issues related to these agrochemical formulations.

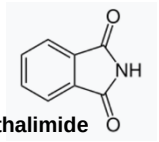
AQUEOUS FOLPET SC AND CAPTAN SC FORMULATIONS

Folpet is a generic contact fungicide of phthalimide class with multisite inhibition activity, widely used individually and in combination with other fungicides for fungi and mold control in fruit, vegetable, and ornamental plant growth. Captan is also a generic contact fungicide of phthalimide class commonly used in agriculture. Aqueous Folpet SC and Captan SC are the widely used formulations, which have several common problems in production and long-term storage. The most painful problems for manufacturers are:

- An unstable pH of the aqueous formulation, which decreases to very low values (1.5-2) during storage, and which is difficult to control during preparation.
- Viscosity, which is unstable in long-term storage, and which is very difficult to control during production.
- Decreasing concentration of the active substance in storage.
- Possible bloating of the packages during storage.

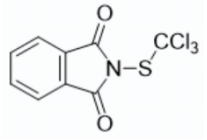
The source of the problems arising during and after formulation production lies in the common synthetic route for technical Folpet and Captan.

Folpet is a fungicide of phthalimide class:

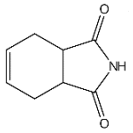


Phthalimide

The molecular structure of Folpet is:

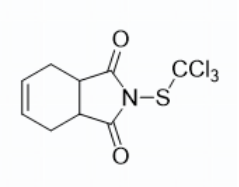


Captan is also a fungicide of phthalimide class with similar structure:

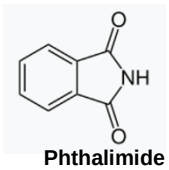


1,2,3,6 Tetrahydrophthalimide (THPA)

Molecular structure of Captan is:



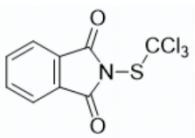
The common route for synthesis of Folpet is as follows (1):



Phthalimide

+ NaOH + $CSCl_4$ =

Perchloro Methyl Mercaptan (PCMM)



Folpet

+ NaCl + H_2O (1)

The common route for the synthesis of Captan is like Folpet but starting with THPA instead of Phthalimide in the case of Folpet.

PERCHLORO METHYL MERCAPTAN

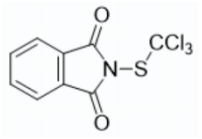
The use of Perchloro Methyl Mercaptan (PCMM) **$CSCl_4$** in Folpet / Captan synthesis has far-reaching consequences. In technical Folpet and Captan from most manufacturers, **PCMM remains as a contamination. This contaminant can sometimes reach 0.5% of the technical substance.**

Both active ingredients and PCMM are hydrolyzed in the aqueous environment.

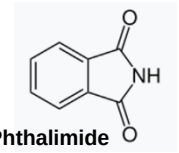
Folpet and Captan **hydrolyze slowly at ordinary temperatures** and pH 2–6, and rapidly at high temperatures or under alkaline conditions. For pH above 7, the reaction depends on pH and has a second-order, i.e., proportional to both concentrations: [A.I.] x [Alkali].

pH 5.5-6.5 is ideal for stabilizing the Folpet SC and Captan SC formulations from the notable hydrolysis of active ingredient (A.I.).

In the alkaline environment, Folpet and Captan are subject to rapid hydrolytic decomposition (2):



$+ 3NaOH =$



Phthalimide

$+ CO_2 + 3NaCl + S + H_2O$ (2)

Captan is finally hydrolyzed to THPA, gaseous Carbon Dioxide, NaCl and S.

Unlike Folpet and Captan, **PCMM is well known as rapidly hydrolyzing in aqueous environment** (3):

$$CSCl_4 + 2H_2O = CO_2 + 4HCl + S \quad (3)$$

and very quickly under high temperatures and alkaline conditions (4):

$$CSCl_4 + 6NaOH = Na_2CO_3 + 4NaCl + S + 3H_2O \quad (4)$$

KNOW-HOW

PCMM CONTAMINATION AS A PROBLEM

*Solid technical Folpet or Captan **with residual PCMM** are not subjected to noticeable hydrolysis in normal storage, but PCMM is hydrolyzed due to residual moisture of solid material and air humidity. As a result of PCMM hydrolysis, the active ingredients immediately show acidity when placed in water, due to the release of HCl and CO_2.*

Some manufacturers add some alkaline agents to the technical Folpet and Captan to neutralize acid emissions during hydrolysis of PCMM. In this case, there is always an excess of a neutralizing alkali agent, but not all PCMM is hydrolyzed when storing solid technical material. The amount of residual PCMM in technical material is a function of the time, storage conditions, and initial PCMM level in A.I. Excess alkaline agent causes alkaline pH when the active ingredient is placed in water.

*During the formulation process, carried out at a normal temperature and in an environment close to neutral, **Folpet and Captan themselves are not notably hydrolyzed, while PCMM immediately starts hydrolysis according to equation (3), if pH is acidic, or according to (4) if pH is alkaline.***

***If pH of the prepared formulation will remain alkaline** due to the use of alkaline A.I. (A.I. with added alkali neutralizing agent), further rapid hydrolysis of both A.I. and PCMM will occur during the storage. A.I. will be hydrolyzed by 2nd order reaction, i.e. proportional to the A.I. concentration multiplied by the alkali concentration. Thus, during storage, the alkali formulation according to equations (2) and (4) will produce NaCl and Na_2CO_3 salts as well as gaseous CO_2.*

Alkali salts have the following negative effects on the formulation:

- *Destabilization of viscosity of the SC formulation – the higher the concentration of salts, the lower and less controlled viscosity is obtained.*

- *Salting out effect for gaseous CO_2 dissolved in water: the higher the salinity of the formulation, the lower the solubility of CO_2 in water. This causes CO_2 to be released from the aqueous formulation, and hence the possibility of the subsequent swelling of sealed packages.*

***If the pH of the prepared formulation is acidic** but not optimal 5.5-6.5 and **not stabilized by a buffer**, then the pH of the formulation in storage will decrease because of PCMM hydrolysis to pH 1-2, which has negative regulatory consequences. Along with this, PCMM will be rapidly hydrolyzed also in an acidic environment, producing CO_2 and HCl.*

It is further hydrolysis of residual PCMM in the formulation that causes subsequent storage problems. HCl causes a decrease in pH, while CO_2 - bloating of packages.

CONCLUSIONS

- ***Thus, if in the final formulation, the pH is not at an optimal level of 5.5-6.5, both when technical A.I. was initially used as acidic and when it was alkaline, and the residual PCMM is more than a few tens ppm, further CO_2 and HCl emissions are inevitable.***
- ***During storage, pH will drop to very low values because of the hydrolysis of the residual PCMM in the formulation, and released CO_2 will create pressure that will cause packages to bloat.***
- ***In the case of a residual alkaline medium in the final formulation, A.I. concentrations will also decrease during storage, along with sharp changes in viscosity. It will totally ruin the product.***

- ***In conclusion, the correct criteria for a successful SC formulation prepared from Folpet or Captan with a residual PCMM content would be:***
    - ***rest of traces of PCMM not more than few tens ppm***
    - ***stable pH during storage with a possible decrease to a pH of not less than 5.5***
    - ***a very small amount of residual CO_2 (because of hydrolysis of traces of PCMM), that will remain dissolved in the water of the formulation with a stable acid pH and will not be released from the formulation.***