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ENVIRONMENTAL CONDITIONS EFFECT ON THE COMMERCIAL FORMULATIONS OF ETHYLENEBISDITHIOCARBAMATE DEGRADATION TO ETHYLENETHIOUREA.

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ABSTRACT

Ethylenethiourea (ETU) is formed during the manufacture of EBDC pesticides such as maneb, mancozeb, metiram, and zineb. It can also be formed during long storage. The influence of some environmental conditions such as temperature, sunlight, ultraviolet (UV) and global warming on the formation of Ethylenethiourea (ETU) was studied for some EBDC formulations. The results demonstrated that the formation of Ethylenethiourea (ETU) was different from each EBDC formulations to another whereas, in the case of Maneb the data showed that the formation of ethylenethiourea was the highest. Moreover, a different behavior during storage in different environmental conditions was noticed, where the storage in greenhouse conditions was higher in the formation of ETU. The percentage increase of ETU in mancozeb, maneb, zineb and metiram formulations was 47.87, 48.04, 48.56 and 46.66% after 144 hours of storage in greenhouse condition, respectively. The percentage increase of ETU in mancozeb, maneb, zineb and metiram formulations was 38.28, 39.10, 35.47and 32.45% after 144 hours of storage at 55°C. Moreover, data showed that the percentage of increase of ETU in mancozeb, maneb, zineb and metiram formulations was 38.77, 40.66, 39.52 and 37.09% after 144 hours of exposure to direct sunlight. Furthermore, the percentage increase of ETU in mancozeb, maneb, zineb and metiram formulations was 22.92, 23.11, 24.77 and 24.02 after 24 hours of exposure to UV-rays.

INTRODUCTION

Ehylenebisdithiocarbamates (EBDCs) are group of non-systemic fungicides which form the most important class of fungicides for controlling important fungal diseases on certain fruits, vegetables and field crops. This class includes mancozeb, maneb, zineb and mitram.

The wide use of ethylenebisdithiocarbamates (EBDCs) in agriculture, poses the problem of potential harm to public health, since it is known that dithiocarbamates and their degradation products contaminate plants, soil and water to various degrees (Arias, and Teresa, 1979).

These fungicides are comparatively safe because of their low mammalian toxicity and very low persistence. The presence of ethylenethiourea is well known neuroteratogen and carcinogen in rodents (Ulland et al 1972, Khera 1987).ETU is present in the commercial formulations as a degradation by-product of the manufacture of EBDCs. It is also formed during product storage and under some environmental conditions (Onley et al 1977, Ripley and Simpson 1977, Rosenberg and Siltanen 1979) has caused great concern.

The present investigation was carried out to reveal the role of, different temperature, sunlight, ultraviolet (UV) light and global warming in the formation of ETU in mancozeb, maneb, zineb and metiram formulations

MATERIALS AND METHODS

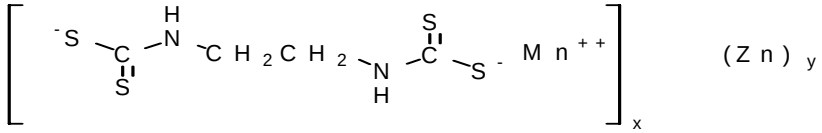
1-Fungicides used: -

1-1-Tridex 80% WP

Common name: mancozeb

IUPAC name: manganese ethylenebisn (dithiocarbamate) (polymeric) complex with zinc salt

Chemical structure:



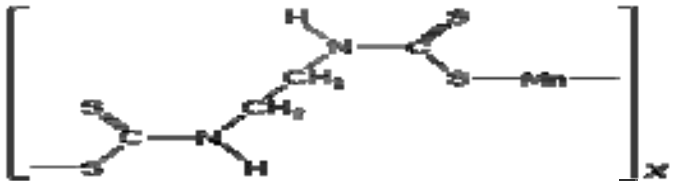
x : y = 1 : 0 . 0 9 1

1-2- Intracol 70% WP

Common name: maneb

IUPAC name: manganese ethylenebis (dithiocarbamate) (polymeric)

Chemical structure:

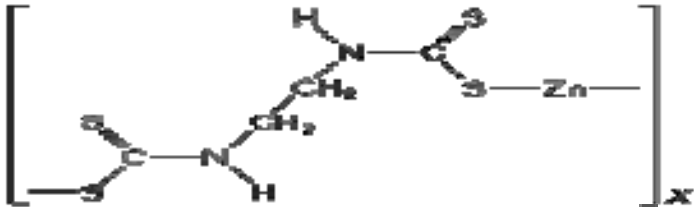


1-3- Zineb 90% Tec

Common name: zineb

IUPAC name: zinc ethylenebis(dithiocarbamate) (polymeric)

Chemical structure:

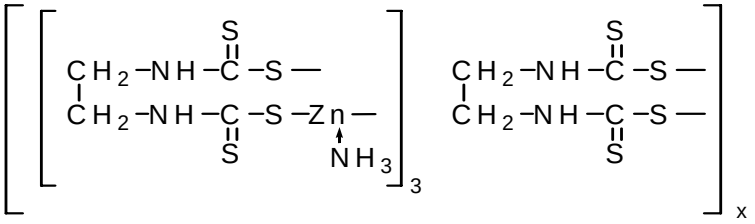


1- 4- Kabritop 60%WG.

Common name: metiram

IUPAC name: zinc ammoniate ethylenebis(dithiocarbamate) - poly(ethylenethiuram disulfide)

Chemical structure:



2-preperation of the deposits:-

One ml methanol containing 10000µg active ingredient of each of; mancozeb, maneb, zineb and metiram was spread as a thin film on the surface of 5cm (i.d) uncovered Petri dishes and the methanol solvent was left to dry. Four groups of these preparations were used.

In order to study the effect of some environmental conditions on the formation of ETU in EBDCs formulations; one group of four uncovered petri-dishes containing deposits were exposed to different temperature 30,35,45 and 50 °C for 0 to 144 hours inside dark electric oven.

Another group of four uncovered Petri-dishes containing the fungicide deposits was exposed to the short wave of the ultraviolet rays 254 nm at 1,3,6,12 and 24 hours. The other group of deposits was exposed to direct sunlight for 1, 4, 8, 12, 24, 48, 96 and 144 hours in July 2010. The last group of deposits was stored under green house condition in July 2010 where the temperature degree ranged from 50 - 55 °C and 80% relative humidity for 1, 4, 8, 12, 24, 48, 96 and 144 hours to study the effect of global warming.

3-Extraction:

Fungicides residues were transferred to glass stopper test tubes using redistilled Methanol as a solvent.

4-Determination of ethylenethiourea (ETU):

ETU in each was extracted by Methanol and determined before and after storage by gas chromatography with flame ionization detector according to the procedure of Haines and Adler (1973).

4-1-GLC conditions:

The type of chromatographic system was Hewlett-Packard serial 6890 gas chromatographic fitted with flame ionization detector (FID), capillary column (15m x 0.53 mm) and the carrier gas was nitrogen at a flow rate of 40 ml/min used under temperature conditions 180, 250, 275 °C for oven, injector and detector, respectively. At these conditions, retention time for ethylenethiourea was 5.3 min. The results of ethylenethiourea were quantitatively determined by comparison with standards of known purity under the identical GLC conditions Haines and Adler (1973).

RESULTS AND DISCUSSION

The data summarized in table (1) indicate the initial ETU content in 10000µg active ingredient of mancozeb, maneb, zineb and metiram which were 23.2, 27.52, 22.24 and 24.56 µg, respectively. These results are in compliance with those obtained by Maneguz and Michalek (1987) whom stated that ETU is present in commercial formulations of EPDCs and it is a major metabolite of ethylenebisdithiocarbamate fungicides which had been reported to be carcinogenic, teratogenic, and mutagenic to the experimental animals (Larsson et al., 1976).

In addition the results show that maneb was the greater in its content of ETU than other candidate fungicides.

On the other hand the data indicate that the initial deposit of ETU in all experimental EBDCs was bellower matching the maximum level 0.5% defined by FAO (1980) whereas the maximum level of ETU as microgram is theoretically 50 µg in 10000 µg active ingredient.

1-Influnce of the different temperature on the formation of ETU in some commercial EBDC formulations:

The data present in Table (1) show that the rate for the formation of ethylenethiourea (ETU) was positive affected with the changing in the temperature. Maneb was more affected by the change in temperature under long period of storge than other tested formulations. The percentage increase of formation of ETU in maneb was 2.14, 5.05 and 8.93 % after one hour of exposure to 35, 45 and 55 °C, respectively, and reached to 19.58, 26.99 and 39.10 % after 144 hours of exposure to these temperatures.

On, the other hand data show that the percentage increases of formation ETU in both zineb 90% Tec and metiram at the end of experiment were 12.98 and 15.39% after exposure to 35°C, respectively. At 45 °C and 55 °C, the same trend was obtained (Table1). Sue Xu (2000) has reported that ethylenethiourea (ETU) was the major degradation product of widely used ethylenebisdithiocarbamate (EBDC) fungicides. Bontoyan and Looker (1973a) studied the effect of storage conditions on the ETU content of formulated EBDC products, and reported that the rate of degradation of EBCDS formation resulting ETU is proportional to the temperature degree.

Table (1): Effect of different temperature degrees on the formation of ETU in EBDCs formulations.

Level of ETU as micrograms and it is percentage increase in EBDCs formulations																								
Exposure time(in hours)	35°C								45° C								55° C							
	Mancozeb		Maneb		Zineb		Metiram		Mancozeb		Maneb		Zineb		Metiram		Mancozeb		Maneb		Zineb		Metiram	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Initial*	23.21	--	27.52	--	22.24	--	24.56	--	23.21	--	27.52	--	22.24	--	24.56	--	23.21	--	27.52	--	22.24	--	24.56	--
6	23.58	1.59	28.11	2.14	22.45	0.94	24.98	1.71	24.33	4.83	28.91	5.05	23.31	4.81	25.41	3.46	25.26	8.83	29.98	8.93	23.87	7.33	26.09	6.22
24	24.25	4.48	28.95	5.31	22.98	3.32	25.62	4.13	25.21	8.61	29.53	7.30	23.77	6.88	26.03	5.98	26.13	12.58	31.36	13.95	24.78	11.42	27.61	12.41
48	25.17	8.44	29.81	8.32	23.57	5.98	26.45	7.69	26.69	14.99	30.93	12.39	24.56	9.45	27.32	11.23	28.07	20.93	33.58	22.02	26.35	18.48	28.92	17.75
96	26.47	14.05	31.64	14.97	24.45	9.94	27.69	12.69	27.91	20.25	32.92	19.62	26.51	19.19	28.18	14.73	30.57	31.71	35.96	30.67	28.53	28.28	30.46	24.02
144	27.26	17.44	32.91	19.58	25.56	12.98	28.34	15.39	29.13	25.50	34.95	26.99	27.66	24.37	30.34	23.53	32.19	38.69	38.28	39.10	30.13	35.47	32.53	32.45

Initial*= one hour before treatment.

2-Influnce of exposure to direct sunlight and storage in green house on the formation of ETU in some EBDCs formulations:

The data present in table (2) show the influence of exposure to direct sunlight and storage in greenhouse condition on formation of ETU in mancozeb, maneb, zineb and meitram formulations. The result obtained revealed that the formation of ETU is significantly influenced by the exposure to direct sunlight of all candidate fungicides where, the percentage increase of ETU in mancozeb, maneb, zineb and metiram formulations was 2.75, 2.63, 2.43 and 2.89% after one hour of exposure and reached to 38.77, 40.66, 39.52 and 37.09% after 144 hours of exposure, respectively. These data are in line with (Rham & Hans Company, 1987c) which studied the aqueous photolysis on mancozeb and reported that, the photolysis half-lives were less than 3 hours with complete disappearance of mancozeb. Identified decomposition products were EBIS, ETU, ethylenediamine (EDA) and EU. Moreover, Fraunhofer 1987 studied the photolysis of maneb in soil and identified decomposition products ofEthyleneurea (EU), ethylenethiourea (ETU), ethylenbis (isothiocyanate) sulfide (EBIS), carbimid, and six unidentified fractions were detected in the methanolic and aqueous fractions.

The data in Table (2) show that the storage in green house condition was more effective in the formation of ETU in all tested EBDC formulations than exposure to direct sunlight. This may due to the high temperature and hight moisture content where, the percentage increase of ETU in mancozeb, maneb, zineb and metiram formulations was 6.51, 5.34, 5.93 and 4.07% after one hour of exposure and reached to 47.87, 48.04, 48.56 and 46.66% after 144 hours of storage in green house condition, respectively. These results are in harmony with those obtained by Lentza-Rizosch (1990) who stated that EBDCs are subject to decomposition at elevated temperature and high humidity and yielding ethylenethiourea (ETU) as the principal metabolite in plants.

Table (2): Effect of Sunlight and global warming on the formation of ETU in EBDCs formulations.

Level of ETU as micrograms and it is percentage increase in EBDCs formulations																
Exposure time(in hours)	Sunlight								Global Warming							
	Mancozeb		Maneb		Zineb		Metiram		Mancozeb		Maneb		Zineb		Metiram	
	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%	µg	%
Initial*	23.21	--	27.52	--	22.24	--	24.56	--	23.21	--	27.52	--	22.24	--	24.56	--
1	23.85	2.75	28.26	2.68	22.78	2.43	25.27	2.89	24.72	6.51	28.99	5.34	23.56	5.93	25.56	4.07
12	24.63	6.12	29.45	7.01	23.87	7.32	26.45	7.69	25.47	9.73	31.86	15.77	25.53	14.79	27.99	13.96
24	26.36	13.57	30.97	12.53	25.12	13.35	28.06	14.25	27.75	19.56	34.36	24.85	27.88	25.36	30.86	25.65
48	27.88	20.12	33.29	20.96	26.98	21.31	29.94	21.91	30.21	30.16	37.13	34.92	30.24	35.97	32.36	31.75
96	29.46	26.92	35.54	29.14	28.35	27.47	31.68	28.99	32.82	41.40	39.45	43.35	32.46	45.95	34.91	42.14
144	32.21	38.77	38.71	40.66	31.03	39.52	33.67	37.09	34.32	47.87	40.74	48.04	33.04	48.56	36.02	46.66

Initial*= one hour before treatment.

3-Influnce of exposure to ultravilote (UV) rays on the formation of Etu in some EBDCs formulations:

Data in Table (3) illustrate that the percentage increase of formation ETU in mancozeb, maneb, zineb and metiram was 3.27, 3.96, 3.46 and 2.40% after one hour of exposure to UV rays, respectively and reached22.92, 23.11 24.77 and 24.02% after 24 hours of exposure at the same sequences.

Generally, from the results it can be demonstrated that storage in green house condition was the more effective in formation of ETU in the all experimental EBDCs formulations than exposure to temperature degree, direct sunlight and UV rays. Furthermore, Maneb was the more affected and was the highest. These results are in line with Nash and Beall, (1980) have stated that the degradation of maneb in air depends on moisture content, temperature, photodegradation, and oxidation.

Table (3): Effect of Ultraviolet light (UV) on the formation of ETU in EBDCs formulations.

Exposure time (in hours)	Level of ETU as micrograms and it is percentage increase in EBDCs formulations							
	Ultraviolet light (UV)							
	Mancozeb		Maneb		Zineb		Metiram	
	µg	%	µg	%	µg	%	µg	%
Initial*	23.21	--	27.52	--	22.24	--	24.56	--
1	23..97	3.27	28.61	3.96	23.01	3.46	25.15	2.40
3	24.52	5.64	29.14	5.88	23.62	6.20	26.28	7.00
6	25.67	10.59	30.22	9.81	24.71	11.10	27.11	10.38
12	26.98	16.24	31.97	16.17	25.64	15.29	28.53	16.16
24	28.53	22.92	33.88	23.11	27.75	24.77	30.46	24.02

Initial*= one hour before treatment.

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التأثير البيئى على التجهيزات التجارية لمبيد ethylenebisdithiocarbamate (EBDCs) و تحولها الى الإثيلين ثيوبوريا (ETU)

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يتم تكوين الإثيلين ثيوريا (ETU) خلال العمليات التصنيعية لمبيدات dithiocrbamate (EBDC) مثل maneb، mancozeb، metiram، zineb. ويمكن أيضا أن يتكون أثناء التخزين و فى هذة الدراسة تم دراسة تأثير بعض الظروف البيئية (درجات الحرارة المختلفة ، و التعرض لاشعة الشمس، الأشعة فوق البنفسجية والاحتباس الحراري) على تكوين الإثيلين ثيوريا (ETU) في بعض مستحضرات EBDC. وكان تكوين الاثيلين ثيويوريا (ETU) يختلف من مركب الى مركب حيث كان maneb أعلى في محتواة من ETU عن مبيدات الثيوكربمات (EBDCs) الأخرى. وأظهرت أيضا سلوك مختلفة أثناء التخزين في ظروف بيئية مختلفة، حيث التخزين في ظروف الصوبة الزراعية كان أكثر فعالية في تكوين ال ETU حيث ان النسبة المئوية للزيادة من ETU في mancozeb، maneb، zineb، metiram كان 87و47-04و48-56و48 -66و46% بعد 144 ساعة من التخزين فى ظروف الصوبة الزراعية على الترتيب . ايضا كانت نسبة الزيادة فى الاثيلين ثيويوريا (ETU) فى سلسلة المبيدات السابقة 28و38- 10و39- 47و35 – 45و32% بعد 144 ساعة من التخزين فى درجة حرارة 55 °م . و بالاضافة الى ذلك فقد اوضحت النتائج ان نسبة الزيادة فى تكوين الاثيلين ثيويوريا (ETU) فى مستحضرات المبيدات السابقة على التوالى كانت 77و38- 66و40- 52و39 – 09و37% بعد 144 ساعة من التعرض لضوء الشمس المباشر ايضا النسبة المئوية للزيادة فى تكوين الاثيلين ثيويوريا (ETU) فى مستحضرات بالترتيب السابق بعد 24 ساعة من التعرض المباشر للاشعة فوق البنفسجية كان 92و22-11و23- 77و24- 02و24% على الترتيب.