



## RESEARCH ARTICLE

## Study the relation between storage and stability of diazinonemulsifiable concentrate formulations in the formation of its impurities and major degradation products

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### Abstract

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In this work, three commercial diazinonemulsifiable concentrate (EC) formulations 60% were collected from the Egyptian market (manufactured from three different companies) to investigate the degradation of diazinon after storage at  $54 \pm 2$  °C for 70 days, at room temperature for 12 months, and exposure to sunlight for 6 months, also identification of some degradation products by GC-MS. In addition to find the causes of the formation of toxicological impurities of diazinon, O,S-TEPP and S,S-TEPP and study the relation between the water content and the amount of impurities. The obtained results showed that, diazinon was more stable after storage at  $54 \pm 2$  °C and at room temperature, while the rate of degradation increased after exposure to sunlight. Analysis of samples after exposure to sunlight using GC-MS identified three degradation products: diazoxon, hydroxydiazinon and 2-isopropyl-6-methyl-4-pyrimidinol (IMP). There was a positive correlation between water content and the amount of O,S-TEPP. Whereas S,S-TEPP didn't affect by storage or water content in diazinon, but it produced during the production process.

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## INTRODUCTION

Diazinon (O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinylphosphorothionate) is a commonly used thionophosphorous organophosphate (OP) pesticide to control a variety of insects in agriculture and household environment (Cox, 1992). Despite its low persistence in the environment, it is a non specific insecticide and highly toxic to animals and humans. Moreover, the toxicity of OPs is increased by their break-down products, which may be bioactivated within an organism or through exposure to the sunlight. The pathway of degradation is assumed to be substitution of sulfur by oxygen in P=S bond, cleavage of the pyrimidine ester bond, and the oxidation of isopropyl group (Koulombos et al., 2003 and Shemer and Linden, 2006). Diazinon undergoes fast hydrolysis at acidic and basic conditions (Mansour et al., 1999 and Zhang and Pehkonen, 1999) in environment, is unstable under UV irradiation (Pehkonen and Zhang, 2002) and can be transformed to the more toxic diazoxon. Its major degradation products are hydroxydiazinon, diazoxon and 2-isopropyl-6-methyl-4-pyrimidinol (IMP) (Koulombos et al., 2003), which may cause acute toxic effects to workers employed in the manufacture and application of this pesticide. Diazinon decomposes at temperatures above 120 °C (NRA, 2002). According to (WHO, 1999), diazinon contains two highly toxic impurities, O,S-TEPP (O, O, Ó, Ó-tetraethyl thiopyrophosphate) and S,S-TEPP (O, O, Ó, Ó-tetraethyl dithiopyrophosphate), moreover the maximum allowed limits of O,S-TEPP in diazinonemulsifiable concentrate is 0.022% and 0.28% for S,S-TEPP of diazinon content. The presence of a small amount of water in acid

medium promotes decomposition to highly toxic by-products O,S-TEPP and S,S-TEPP (NRA, 2002). The aim target of this work is to investigate and study the stability of three commercial diazinon emulsifiable concentrate formulations 60% collected from the Egyptian market (manufactured from three different companies), and the formation of its impurities after storage at different intervals of temperature, also identification of some degradation products after storage in sunlight. The structure of diazinon and its impurities are shown in Fig. (1).

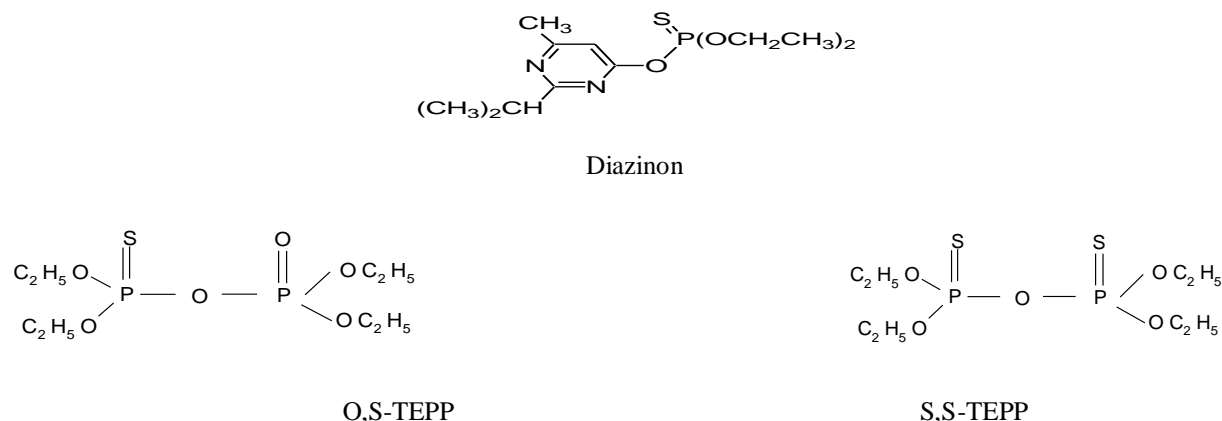


Fig. 1. The structure of diazinon and its impurities

## Material and Methods

### 1. Materials

Diazinon 98%, O,S-TEPP 96% and S,S-TEPP 97.1% were obtained from Chem Service. Diazinon 60% EC (w/v) commercial formulations were obtained from three different Manufacture sources in Egypt (Manufactured from three different companies).

### 2. Methods

#### 2.1. Accelerated storage procedure (CIPAC MT 46, 1995)

Place the emulsifiable concentrate (about 50 ml) in the bottle. Cap the bottle and put it in the oven for specified time and temperature. At the end of the time, remove the bottle from the oven, remove the cap, and allow the bottle and contents to cool naturally to room temperature, replacing the cap when cool.

Storage at  $54 \pm 2^\circ\text{C}$  for 14, 28, 42, 56, 70 days.

Storage in sunlight for 1, 2, 3, 4, 5, 6 months.

Storage at room temperature for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 months.

#### 2.2. Preparation of samples

##### 2.2.1. Diazinon

- Standard Preparation

Weight 10 mg of diazinon analytical standard into a 25ml volumetric flask then dissolve it and complete to the final volume with methanol.

- Sample Preparation

Accurately weight sufficient sample of diazinon formulation 60% w/v to equivalent 10 mg of diazinon standard into a 25 ml volumetric flask mix slowly with methanol and complete the volume with methanol.

##### 2.2.2. O,S-TEPP and S,S-TEPP

- Standard preparation

Weight 10 mg of O,S-TEPP analytical standard into a 25 ml volumetric flask dilute to volume with methanol and mix., and by the same method prepare S,S-TEPP standard solution.

- Sample Preparation

Accurately weight sufficient sample material formulation to contain approximately 1 mg diazinon into a 25 ml volumetric flask, dilute to volume with methanol and mix.

### 3. Measurements

#### 3.1. Gas Chromatography Determination for diazinon, O,S-TEPP and S,S-TEPP (WHO, 1999)

Agilent 7890A gas chromatograph equipped with Flame Ionization Detector (FID) at 300 °C, capillary column HP-50+(30 m x 0.53 mm I.D., 1 µm film thickness). Nitrogen was used as a carrier gas at 20 ml/min. The oven temperature program was held at 160 °C for 1 min, then ramp 25 °C /min to 260 °C, and kept at that temperature for 5 min. Injector temperature was 250 °C. The injection volume was 1 µl. under these conditions the typical retention times of diazinon, O,S-TEPP and S,S-TEPP were 4.13, 3.5 and 3.6 min., respectively.

#### 3.2. Gas chromatography-mass spectrometry analysis of diazinon

The GC-MS analysis was performed with an Agilent 6890 gas chromatograph equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS(30 m x 320 µm x 0.25 µm film thickness). Helium was used as carrier gas at approximately 1.0 ml/min pulsed splitless mode. The solvent delay was 3 min, and the injection volume was 1 µl. The mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of 70 e.v scanning from m/z 50 to 500. The ion source temperature was 230 °C and the quadrupole temperature 150 °C. The electron multiplier voltage (EM voltage) was maintained 1050 v above auto tune. The instrument was manually tuned using perfluorotributyl amine (PFTBA). The GC temperature program was held at 80 °C for 3 min, then elevated to 260 °C at rate of 8 °C/min, the detector and injector temperature were set at 280 and 250 °C, respectively.

#### 3.3. Determination of water content (CIPAC MT 30.2, 1995)

The apparatus consists of a glass flask (A) connected by a tube (D) to a cylindrical tube (B) fitted with a graduated receiving tube (E) and a reflux condenser (C). The receiving tube (E) is graduated in 0.1 ml divisions so that the error of reading doesn't exceed 0.05 ml. The preferred source of heat is an electrical heater with rheostat control. The upper portion of the flask and the connecting tube may be insulated. Thoroughly clean the receiving tube and the condenser of the apparatus rinse with water and dry. Introduce 200 ml of toluene R and about 2 ml of water into a dry flask. Heat the flask to distil the liquid over a period of 2 hour, allow cooling for about 30 min. and reading off the volume of water to an accuracy of 0.05 ml (first distillation). Weigh accurately a quantity of the material expected to give about 2-3 ml of water and transfer to the flask gently for 15 min. When boiling begins, distillate rate of 2 drops per second until most of the water has distilled over, then increase the rate of distillation to about 4 drops per second. As soon as the water has been completely distilled, rinse the inside of the condenser tube with toluene B. Continue the distillation for 15 minute, remove the heat, allow the receiving tube to cool to room temperature and dislodge tube by tapping the tube. Allow the water and toluene layers to separate and read off the volume of water, (second distillation).

Calculate the content of water as g/kg using the formula:

$$1000 \times (N_1 - N) / W$$

Where:

W = the weight in g of the material being examined.

N = the number of ml of water obtained in the first distillation.

N<sub>1</sub> = the total number of ml of water obtained in both distillations.

## Result and Discussion

### 1. Effect of storage Stability on diazinon 60% EC content.

Data from Table (1) showed the effect of storage at 54 ± 2 °C on three commercial diazinon formulations and indicated that, diazinon has not been changed by storage at 54 ± 2 °C for 14, 28, 42 days, for sources I and III, but there was a change in diazinon content of source II at 28 and 42 days indicating 3.40 and 5.37 loss percentages respectively. The loss percentages were increased to reach 4.69, 9.24 and 3.81% for sources I, II and III after storage for 70 days, respectively. However diazinon was more stable after storage at room temperature and the loss percentages after 12 months were 1.65, 3.60 and 2.20% for sources I, II, and III, respectively Table (2). Diazinon was less stable after storage in sunlight and the loss percentages after 6 months were found to be 11.21, 23.99 and 8.94% for source I, II, and III, respectively Table (3). The previously mentioned results clearly showed that the rate of degradation of the three diazinon formulations under investigation were influenced by change in temperature degrees and long period of storage, moreover there is a very clear effect of storage in the sun, and the rate of

degradation of diazinon was more and faster than the storage at  $54 \pm 2$  °C and at room temperature (Tables; 1, 2, and 3). Our findings are in harmony with these obtained by several investigators (Ola and Shereen, 2007 and Ola, 2012), reported that diazinon was more stable after storage at  $54 \pm 2$  °C for 14 days and this achieved in this study.

The samples of diazinon were analyzed after storage in sunlight using GC-MS to identify the degradation products, and found that the characteristic ions at  $m/z$  304, 320, 290 and 152 were molecular ions of diazinon, hydroxydiazinon, diazoxon and IMP (Fig.,2). Diazinon is rapidly hydrolyzed at low or high pH values since it is susceptible to both base and acid catalyzed hydrolysis (Freed et al., 1979) Hydrolysis is the major process in degradation of diazinon and the main degradation product is IMP (Bavcon et al., 2003 and Basfar et al., 2007). The analysis of our samples using GC-MS found that diazinon can be hydrolysed to IMP  $m/z$ , 152 which in accordance with the hydrolysis. Phosphorus oxygen bond was cleaved to generate IMP (Kouloumbos et al., 2003; Bavcon et al., 2003 and Basfar et al., 2007).

Also analysis of our samples using GC-MS found that the characteristic ion at  $m/z$ , 290 [M+2] was molecular ion of diazoxon. Diazinon can be oxidized to diazoxon, and it can be formed by the substitution of sulfur by oxygen on P=S bond, and this was agreement with (Kouloumbos et al., 2003). In addition to results from GC-MS revealed that the characteristic ion at  $m/z$ , 152 was molecular ion of IMP and this is another possibility for the existence of IMP and this was agreement with (Basfar et al., 2007) who reported that the diazoxon may also hydrolyze to IMP, and this can be shown according to possible degradation pathways of diazinon in Fig (2).

Moreover results from the analysis of our samples using GC-MS showed that the characteristic ion at  $m/z$ , 320 was molecular ion of hydroxydiazinon, and these results were agreement with (Zhang et al., 2011) who reported that hydroxylation at the tertiary and primary carbon atoms of the isopropyl group occurred and resulted in the formation of hydroxydiazinon and 2- hydroxydiazinon, and this can be shown according to possible degradation pathways of diazinon in Fig (2).

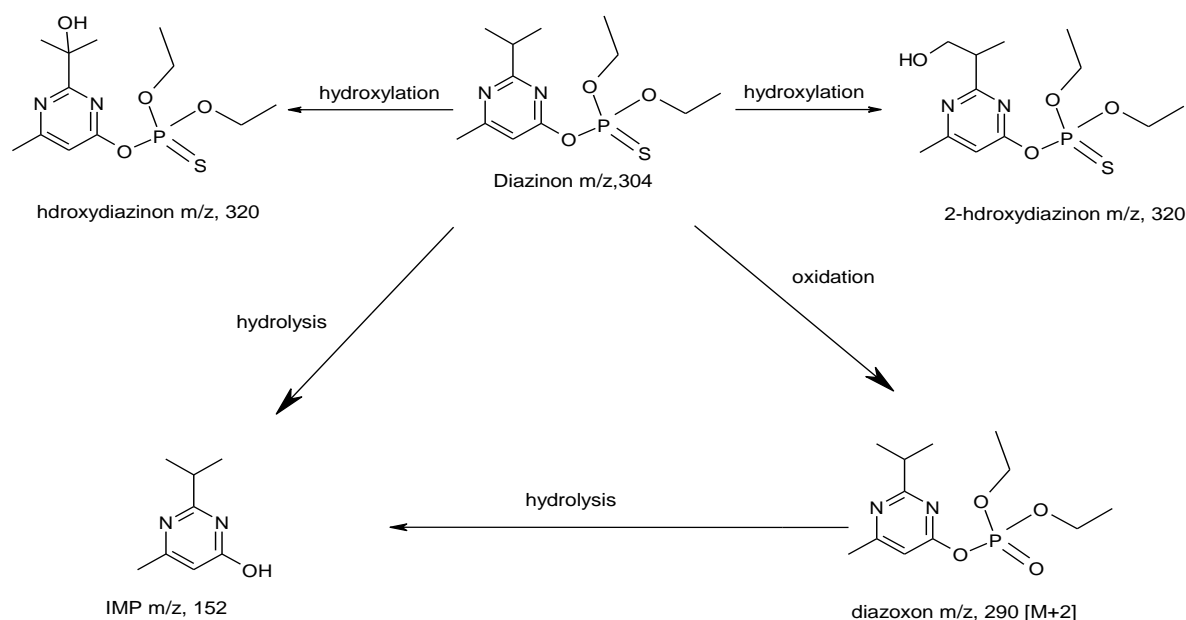


Fig. 2. Possible degradation pathways of diazinon

Table (1): Effect of storage stability on Diazinon 60% EC of three different manufactured sources at 54±2°C.

Storage Periods (Days)	Source I		Source II		Source III	
	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %
0	59.86	0	59.93	0	59.87	0
14	59.78	0.13	58.83	1.84	59.63	0.40
28	59.38	0.80	57.89	3.40	59.47	0.67
42	58.98	1.47	56.71	5.37	59.05	1.37
56	57.33	4.22	55.68	7.09	58.76	1.85
70	56.89	4.96	54.39	9.24	57.59	3.81

Table (2): Effect of storage stability on Diazinon60% EC of three different manufactured sources at room temperature.

Storage Periods (months)	Source I		Source II		Source III	
	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %
0	59.86	0	59.93	0	59.87	0
1	59.78	0.13	59.90	0.05	59.72	0.25
2	59.55	0.52	59.65	0.47	59.61	0.43
3	59.47	0.65	59.57	0.60	59.53	0.57
4	59.22	1.07	59.33	1	59.49	0.63
5	59.15	1.19	58.97	1.60	59.34	0.86
6	59.01	1.42	58.83	1.84	59.22	1.09
7	58.99	1.45	58.82	1.85	59.09	1.30
8	58.96	1.50	58.72	2.02	58.99	1.47
9	58.95	1.52	58.57	2.27	58.94	1.55
10	58.89	1.62	58.06	3.12	58.84	1.72
11	58.89	1.62	57.95	3.30	58.72	1.92
12	58.87	1.65	57.77	3.60	58.55	2.20

Table (3): Effect of storage stability on Diazinon 60% EC of three different manufactured sources in sunlight.

Storage Periods (months)	Source I		Source II		Source III	
	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %	Diazinon content (w/v) %	Loss %
0	59.86	0	59.93	0	59.87	0
1	59.49	0.62	58.19	2.90	59.69	0.30
2	57.08	4.64	56.61	5.54	58.87	1.67
3	56.67	5.33	55.27	7.78	58.26	2.69
4	55.59	7.13	54.36	9.29	57.65	3.71
5	54.37	9.17	51.09	14.75	56.74	5.23
6	53.15	11.21	45.55	23.99	54.52	8.94

## 2. Effect of storage stability on the formation of impurities.

Data presented in Tables (4, 5, 6) showed that the effect of storage on the amount of O,S-TEPP and S,S-TEPP at  $54 \pm 2$  °C for sources I,II and III. The results indicated that the amount of O,S-TEPP before storage was 0.503 g/kg for source I and it was undetectable for sources II and III, and there was no change in the amount of O,S-TEPP after storage for 70 days at  $54 \pm 2$  °C. The maximum level of O,S-TEPP in diazinonemulsifiable concentrate is 0.022% of diazinon content. Obtained results showed that the maximum level after 70 days from storage was 0.123, 0.119 and 0.125 g/kg for sources I,II and III, respectively. From these obtained results, the amount of O,S-TEPP was more than the maximum allowed limits before and after storage for source I. For S,S-TEPP there was, however no change in the results before and after storage for the tested three sources. The amounts of S,S-TEPP before storage were 0.861, 1.03 and 0.604 g/kg for sources I,II and III respectively, and after storage for 70 days at  $54 \pm 2$  °C recorded 0.961, 1.28 and 0.413 g/kg for source I,II and III, respectively. Also the amount of S,S-TEPP was in allowed limits for all sources, where the maximum level of S,S-TEPP in diazinonemulsifiable concentrate is 0.28% of diazinon content. From the obtained results the maximum levels after storage for 70 days at  $54 \pm 2$  °C were 1.561, 1.510 and 1.592 g/kg for sources I,II and III, respectively.

The data from Tables (7, 8, 9) showed the effect of storage for 12 months on the amounts of O,S-TEPP and S,S-TEPP at room temperature for sources I,II and III. The results indicated that the amounts of O,S-TEPP after storage for 12 months were 0.619, 0.125 and 0.132 g/kg for sources I,II and III respectively, where the maximum levels of O,S-TEPP were 0.127, 0.126 and 0.127 g/kg for sources I,II and III, respectively. From these obtained results the amount of O,S-TEPP was more than the maximum allowed limits after storage for sources I and III. For S,S-TEPP also there was no change in the results before and after storage for the three tested sources and it was in allowed limits for all sources, where the amounts of S,S-TEPP after storage for 12 months were 1.17, 1.21, and 0.303 g/kg for sources I,II and III respectively, where the maximum levels of S,S-TEPP were 1.616, 1.604 and 1.618 g/kg for sources I,II and III, respectively.

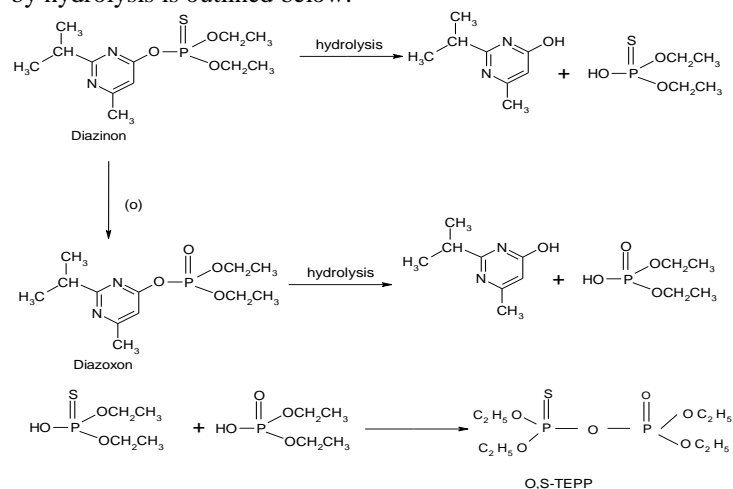
The data from Tables (10, 11, 12) showed the effect of exposure of diazinon to sunlight for 6 months on the amount of O,S-TEPP and S,S-TEPP for sources I,II and III. The results indicated that the amounts of O,S-TEPP after storage for 6 months were 0.497, 0.281 and 0.284 g/kg for source I,II and III, respectively, where the maximum levels of O,S-TEPP were 0.115, 0.099 and 0.118 g/kg for source I,II and III respectively. From these obtained result

, the amount of O,S-TEPP was more than the maximum allowed limits after storage for all sources .For S,S-TEPP there was no change in the results before and after storage for sources I and III ,and there was little change in the amount of S,S-TEPP for source II after storage for 6 months in sunlight . The amounts of S,S-TEPP after storage for 6 months were 1.17 ,2.37 and 0.303 g/kg for source I ,II and III, respectively ,where the maximum levels of S,S-TEPP were 1.459 ,1.264 and 1.507 g/kg for source I ,II and III, respectively . From these obtained results the amount of S,S-TEPP was more than the maximum allowed limits after storage for source II .

The previously mentioned results clearly showed that the amounts of O,S-TEPP and S,S-TEPP in diazinon formulation from the three tested sources were affected by many factors such as manufacturing process , sources of starting materials, exposure to air, light and elevated temperature, and also hydrolysis, particularly if diazinon formulation contains a small amount of water can lead to form O,S-TEPP and S,S-TEPP .To find the causes of formation of O,S-TEPP and S,S-TEPP, water amount was determined in all samples of diazinon in all intervals .

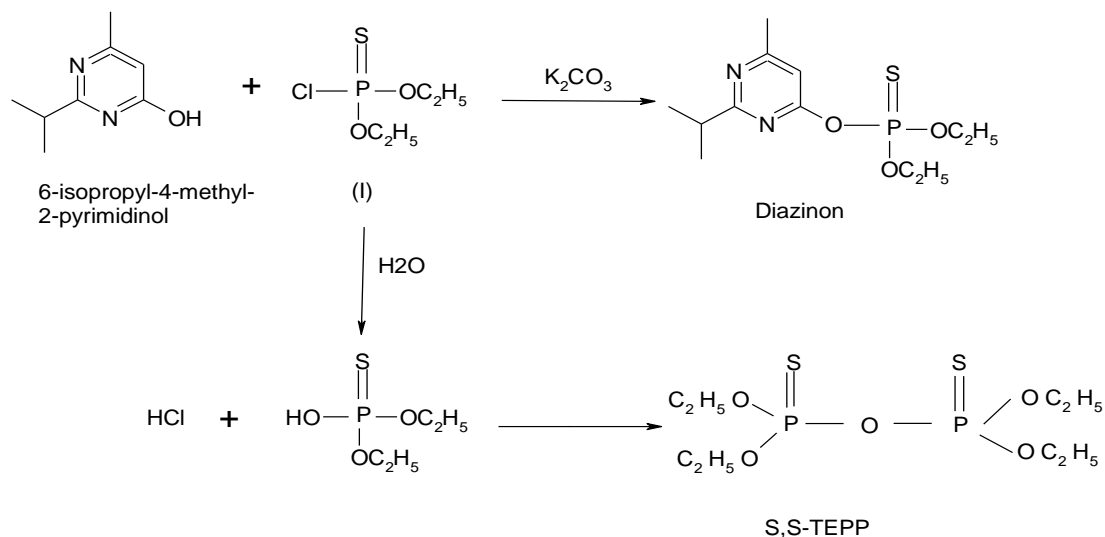
Data from Tables (4, 5, 6) showed that the water content (g/kg) for three sources of diazinon at  $54 \pm 2$  °C for 70 days , the results indicated that water contents were 2.17 ,0.766 and undetectable for source I ,II and III, respectively . From these results it was found that there is a positive correlation a relation between the water content and formation of O,S-TEPP . According to (WHO, 1999) the maximum allowed limits of water in diazinon is 2 g/kg. From our results the water content in diazinon for source I was more than the allowed limits so the amount of O,S-TEPP before and after storage was more than the allowed limits for water content . Also the data from Tables (7, 8, 9) showed that the water content (g/kg) for three used sources of diazinon at room temperature for 12 months, the results indicated that increasing of water content for source I didn't affect on the amount of O,S -TEPP ,but when the water appeared after 6 months from storage, it affected on the amount of O,S-TEPP, and also occurred after storage in sunlight and data in Tables (10, 11, 12) showed this.

From the mentioned results we can find the formation of toxic impurities in diazinon. In excess of water the principal products of hydrolysis of diazinon are diethyl thiophosphoric acid and 2-isopropyl-4-methyl-6-hydroxypyrimidine. On the other hand, the presence of only trace amounts of water leads to the formation of the O,S-TEPP. The initial hydrolysis of diazinon gives diethyl thiophosphoric acid and 2-isopropyl-4-methyl-6-hydroxypyrimidine. The diazinon undergoes oxidation and hydrolysis to diethylphosphoric acid, which subsequently combines with diethylthiophosphoric acid to form the O,S-TEPP. The proposed mechanism of oxidation followed by hydrolysis is outlined below:



In addition to the previously mentioned results clearly showed that the amount S,S-TEPP didn't affected by storage at  $54 \pm 2$  °C at room temperature and exposure to sunlight and that for the three manufactured sources of diazinon formulations , also S,S-TEPP content was in allowed limits according to WHO (1999), where the maximum level of S,S-TEPP in diazinonemulsifiable concentrate is 0.28% of diazinon content. The concentration of S,S-TEPP was not a function of the age of the formulation , the oldest sample has a S,S-TEPP concentration lower than source of the other formulation samples analyzed , that S,S-TEPP can be produced during the production process of diazinon. The following equation gave explanation for the above mentioned results:





Also these obtained results are in agreement with (NRA, 2002; Toy, 1951; Meier et al., 1979 and Ambrus et al., 2003).

Table (4): Effect of storage on the amount of impurities in diazinon 60 % EC from source I at  $54 \pm 2^\circ\text{C}$

Storage Periods (Days)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	586.71	0.129	0.295	1.643	0.505	0.503	0.861	2.17
14	585.92	0.129	0.277	1.641	0.508	0.473	0.867	2.17
28	582.003	0.128	0.309	1.629	0.509	0.531	0.875	2.16
42	578.08	0.127	0.306	1.619	0.520	0.529	0.899	2.15
56	561.91	0.124	0.301	1.573	0.535	0.536	0.952	2.15
70	557.60	0.123	0.295	1.561	0.536	0.529	0.961	2.17

Table (5): Effect of storage on the amount of impurities in diazinon 60 % EC from source II at 54±2°C

Storage Periods (Days)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	594.23	0.131	-	1.664	0.614	-	1.03	0.501
14	583.32	0.128	-	1.633	0.623	-	1.07	0.511
28	574.004	0.126	-	1.607	0.635	-	1.11	0.628
42	562.30	0.124	-	1.574	0.639	-	1.14	0.666
56	552.09	0.121	-	1.546	0.668	-	1.21	0.753
70	539.30	0.119	-	1.510	0.693	-	1.28	0.766

Table (6): Effect of storage on the amount of impurities in diazinon 60 % EC from source III at 54±2°C

Storage Periods (Days)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	590.96	0.130	-	1.655	0.357	-	0.604	-
14	588.59	0.129	-	1.648	0.356	-	0.605	-
28	587.01	0.129	-	1.644	0.331	-	0.564	-
42	582.86	0.128	-	1.632	0.271	-	0.465	-
56	580.002	0.128	-	1.624	0.258	-	0.445	-
70	568.45	0.125	-	1.592	0.235	-	0.413	-

Table (7): Effect of storage on the amount of impurities in diazinon 60 % EC from source Iat roomtemperature.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	586.71	0.129	0.295	1.643	0.505	0.503	0.861	2.17
1	585.92	0.129	0.296	1.641	0.585	0.505	0.998	2.17
2	583.67	0.128	0.302	1.634	0.610	0.517	1.05	2.17
3	582.88	0.128	0.313	1.632	0.616	0.537	1.06	2.17
4	580.43	0.128	0.285	1.625	0.619	0.491	1.07	2.35
5	579.75	0.128	0.288	1.623	0.623	0.497	1.07	2.39
6	578.38	0.127	0.308	1.619	0.633	0.533	1.09	2.40
7	577.18	0.127	0.312	1.619	0.640	0.539	1.11	2.40
8	577.89	0.127	0.320	1.618	0.641	0.554	1.11	2.41
9	577.79	0.127	0.332	1.618	0.652	0.574	1.13	2.45
10	577.20	0.127	0.347	1.616	0.666	0.601	1.15	2.47
11	577.20	0.127	0.355	1.616	0.667	0.615	1.16	2.51
12	577.004	0.127	0.357	1.616	0.674	0.619	1.17	2.60

Table (8): Effect of storage on the amount of impurities in diazinon 60 % EC from source II at room temperature.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	594.23	0.131	-	1.664	0.614	-	1.03	0.501
1	593.93	0.131	-	1.663	0.615	-	1.035	0.501
2	591.45	0.130	-	1.665	0.620	-	1.05	0.503
3	590.66	0.130	-	1.654	0.625	-	1.06	0.525
4	588.28	0.129	-	1.647	0.627	-	1.07	0.533
5	584.71	0.129	-	1.637	0.632	-	1.08	0.543
6	583.32	0.128	-	1.633	0.644	-	1.10	0.756
7	583.23	0.128	0.0201	1.633	0.651	0.034	1.12	0.978
8	582.23	0.128	0.0311	1.633	0.659	0.053	1.13	1.14
9	580.75	0.128	0.0452	1.626	0.668	0.078	1.15	1.25
10	575.69	0.127	0.0519	1.612	0.673	0.090	1.17	1.29
11	574.60	0.126	0.0637	1.609	0.687	0.111	1.19	1.37
12	572.81	0.126	0.0718	1.604	0.693	0.125	1.21	1.68

Table (9): Effect of storage on the amount of impurities in diazinon 60 % EC from source III at room temperature.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	590.96	0.130	-	1.655	0.357	-	0.604	-
1	589.48	0.130	-	1.650	0.379	-	0.643	-
2	588.39	0.129	-	1.647	0.393	-	0.668	-
3	587.60	0.129	-	1.645	0.350	-	0.596	-
4	587.21	0.129	-	1.644	0.256	-	0.436	-
5	585.73	0.129	-	1.640	0.250	-	0.427	-
6	584.54	0.129	-	1.637	0.246	-	0.421	-
7	583.26	0.128	0.0110	1.633	0.236	0.0189	0.405	0.118
8	582.27	0.128	0.0350	1.630	0.225	0.0601	0.386	0.118
9	581.78	0.128	0.0415	1.629	0.214	0.0713	0.368	0.118
10	580.79	0.128	0.0532	1.626	0.194	0.0916	0.334	0.121
11	579.61	0.128	0.0645	1.623	0.183	0.111	0.316	0.121
12	577.93	0.127	0.0765	1.618	0.175	0.132	0.303	0.131

Table (10): Effect of storage on the amount of impurities in diazinon 60 % EC from source I in sunlight.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	586.71	0.129	0.295	1.643	0.505	0.503	0.861	2.17
1	583.08	0.128	0.251	1.633	0.523	0.430	0.897	2.60
2	559.46	0.123	0.271	1.566	0.530	0.484	0.947	2.75
3	555.44	0.122	0.267	1.555	0.599	0.481	1.08	2.87
4	544.86	0.120	0.273	1.526	0.607	0.501	1.11	3.11
5	532.90	0.117	0.277	1.492	0.609	0.520	1.14	3.27
6	520.94	0.115	0.259	1.459	0.610	0.497	1.17	3.55

Table (11): Effect of storage on the amount of impurities in diazinon 60 % EC from source II in sunlight.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	594.23	0.131	-	1.664	0.614	-	1.03	0.501
1	576.98	0.127	0.0792	1.616	0.718	0.137	1.24	0.705
2	561.31	0.123	0.0833	1.572	0.751	0.148	1.34	0.969
3	548.03	0.121	0.0924	1.534	0.789	0.169	1.44	1.35
4	539.002	0.119	0.112	1.509	0.835	0.208	1.55	1.66
5	506.58	0.111	0.119	1.418	1.07	0.235	2.11	2.25
6	451.65	0.099	0.127	1.264	1.072	0.281	2.37	3.66

Table (12): Effect of storage on the amount of impurities in diazinon 60 % EC from source III in sunlight.

Storage Periods (months)	Diazinon content g/kg	Maximum of O,S-TEPP 0.022% of Diazinon content g/kg	O,S-TEPP found g/kg	Maximum of S,S-TEPP 0.28% of Diazinon content g/kg	S,S-TEPP found g/kg	Impurities as g/kg of Diazinon content		Water content g/kg
						O,S-TEPP found g/kg	S,S-TEPP found g/kg	
0	590.96	0.130	-	1.655	0.357	-	0.604	-
1	589.18	0.130	-	1.650	0.317	-	0.538	-
2	581.09	0.128	-	1.627	0.226	-	0.389	-
3	575.07	0.126	-	1.610	0.208	-	0.362	-
4	569.05	0.125	0.0718	1.593	0.188	0.126	0.330	0.151
5	560.06	0.123	0.134	1.568	0.179	0.239	0.320	0.337
6	538.15	0.118	0.153	1.507	0.163	0.284	0.303	0.755

## References

- Ambrus, A.; Hamilton, D. J.; Kuiper, H. A.; Racke, K. D.; 2003.** Significance of impurities in the safety evaluation of crop protection products. *Pure Appl. Chem.*, 75(7): 937-973.
- Basfar, A.A.; Mohamed, K.A.; Al-Abduly, A.J.; Al-Kuraiji, T.S.; Al-Shahrani, A.A.; 2007.** Degradation of diazinon contaminated waters by ionizing radiation. *Journal of Radiation Physics and Chemistry*. 76: 1474-1479.
- Bavcon, M.; Trebse, P.; Zupancic-Kralj, L.; 2003.** Investigation of the determination and transformations of diazinon and malathion under environmental conditions using gas chromatography coupled with a flame ionization detector. *Chemosphere* 50: 595-601.
- CIPAC MT 46 (1995).** Collaborative International Pesticides Analytical Council (CIPAC); Accelerated Storage Procedure; Vol., F, p. 148-151.
- CIPAC MT 30.2 (1995).** Collaborative International Pesticides Analytical Council (CIPAC); Dean and Stark method; Vol., F, p. 93-94.
- Cox, C.; 1992.** Diazinon. *Journal of pesticide Reform* 12(3): 30-35.
- Freed, V.H.; Chiou, C.T.; Schmedding, D.W.; 1979.** Degradation of selected organophosphate pesticides in water and soil. *J. Agric. Food Chem.* 27: 706-708.
- Kouloumbos, V.N.; Tsipi, D.F.; Hiskia, A.E.; Nikolic, D.; vanBremen, R.B.; 2003.** Identification of photocatalytic degradation products of diazinon in TiO<sub>2</sub> aqueous suspensions using GC/MS/MS and LC/MS with quadrupole time-of-flight mass spectrometry. *Journal of the American Society for Mass Spectrometry* 14(8): 803-817.
- Mansour, M.; Feicht, E.A.; Behecti, A.; Schramm, K.W.; Kettrup, A.; 1999.** Determination photostability of selected agrochemicals in water and soil. *Chemosphere* 39: 575-585
- Meier, E. P.; Dennis, W. H.; Rosencrance, A. B.; Randall, W. F.; Cooper, W. J.; Warner, M. C.; 1979.** Sulfotepp, a toxic impurity in formulations of diazinon. *Bull. Environ. Contam. Toxicol.*, 23: 158-164.
- NRA (2002).** National Registration Authority for Agricultural and veterinary chemicals, Review of diazinon, volume 2.
- Ola, M.Y.Emara; 2012.** Toxic impurities in some commercial formulations of Dimethoate, Diazinon, and Chlorpyrifos-methyl. *J. Biol. Chem. Environ. Sci.*, 7(1): 167-188.
- Ola, M.Y.Emara; Shereen, A. Abd El-Azziz; 2007.** Effect of storage temperature on the stability of chemical and physical properties of certain local organophosphorus insecticide formulations. *Egypt J. of Appl. Sci.*, 22(2B): 813-828.
- Pehkonen, S.O.; Zhang, Q.; 2002.** The degradation of organophosphorus pesticides in natural waters: A critical review. *Critical Reviews in Environmental Science and Technology* 32: 17-72.
- Shemer, H.; Linden, K.G.; 2006.** Degradation and by-product formation of diazinon in water during UV and UV/H<sub>2</sub>O<sub>2</sub> treatment. *Journal of Hazardous Material* 136: 553-559.
- Toy, A. D. F.; 1951.** *J. Am. Chem. Soc.*, 73: 4670-4674.



**WHO (1999).** World Health Organization Specifications for Diazinon.

**Zhang, Q.; Pehkonen, S.O.; 1999.** Oxidation of diazinon by aqueous chlorine: kinetics, mechanisms, and product studies. *Journal of Agricultural and Food Chemistry* 47: 1760–1766.

**Zhang, Y.; Hou, Y.; Chen, F.; Xiao, Z.; Zhang, J.; Hu, X.; 2011.** The degradation of chlorpyrifos and diazinon in aqueous solution by ultrasonic irradiation: Effect of parameters and degradation pathway. *Chemosphere* 82: 1109-1115