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Archives of Applied Science Research, 2013, 5 (2):241-250
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ISSN 0975-508X
CODEN (USA) AASRC9

UV stabilization of simazine technical and its formulation by using different packaging materials and inorganic compound TiO_2 as UV stabilizer

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ABSTRACT

Simazine is 1,3,5- triazine herbicide molecules (an organic herbicide). Its technical and formulation was found to stabilize against UV light and sunlight by using Titanium dioxide as UV Stabilizer. Successful use of inorganic UV stabilizer in the pesticide formulations, like Simazine is UV unstable herbicide , which degrades by sunlight and UV rays exposer. Titanium dioxide (TiO_2) is well known UV stabilizer used in cosmetics and plastic industry very widely for the stabilization. Brown PET (Polyethylene Ter phthalate) bottles as packaging materials plays important role in stabilizing the technical and it's formulations along with the TiO_2 as UV stabilizer as compared to the white HDPE bottles.

Keywords: Titanium dioxide (TiO_2), Simazine, Inorganic UV stabilizer, PET bottles and HDPE bottles.

INTRODUCTION

Simazine is a photosynthetic electron transport inhibitor at the photosystem II receptor site. Maize tolerance of triazines is attributed to conjugation with glutathione. Its mode of action is selective systemic herbicide, absorbed principally through the roots, but also through the foliage, with translocation acropetally in the xylem, accumulating in the apical meristems and leaves. Under field conditions, simazine has a low leaching potential. Loss by direct photodecomposition is insignificant. Indirect photodecomposition in the presence of photo sensitisers such as humic acids is, however, likely [1].

Simazine is susceptible to degradation or decomposition by UV light , Photodegradation of triazine herbicides in aqueous solutions and natural waters was studied by Evgenidou, E.; Fytianos, K. [2]. The photodegradation of three triazines, atrazine, simazine, and prometryn, in aqueous solutions and natural waters using UV radiation ($\lambda > 290$ nm) has been studied. Experimental results showed that the dark reactions were negligible. The rate of photodecomposition in aqueous solutions depends on the nature of the triazines and follows first-order kinetics. Abiotic persistence of atrazine and simazine in water was studied by Comber, Sean D. W.[3] .Hydrolysis and photolysis experiments have been undertaken to investigate the abiotic persistence of atrazine and simazine in a variety of waters. Hydrolysis only occurs to a significant extent at pH values at the lower limit of those found in the natural aquatic environment (pH 4.0 or less). Photolysis was initiated by a wide range of wavelengths in waters at pH 4.0, but only by more energetic wavelengths of less than 300 nm at higher pH values (pH 6 to 8) .In ground waters, atrazine and simazine will have half-lives in the order of years, due to the exceedingly slow rate of hydrolysis . Effect of sunlight on the phytotoxicity of some phenylurea and triazine herbicides on a soil surface was studied by Jordan, L.S.et.al [4]. Sterilized soil in metal cans was treated with the herbicide and exposed to normal sunlight for 25-60 days. The soils were mixed, diluted to various degrees and oats planted. Herbicides used were atrazine, simazine, diuron, monuron, and fenuron. All showed reduced phytotoxicity after 25 days, even when soil temperature did not exceed 49°. Simazine lost toxicity in the dark after 60 days. When held at 82° in sunlight, all lost 65-97% of their toxicity. Semiconductor-sensitized photo degradation of s-triazine and chloroacetanilide herbicides in leaching water using TiO_2 and ZnO as catalyst under natural sunlight was studied by Fenoll et.al [5] . In the present study, the photo catalytic degradation of five s-triazine (simazine, prometryn, terbutryn, atrazine and terbuthylazine) and three chloroacetanilide (propachlor, s-metolachlor, alachlor) herbicides in leaching water has been investigated. Zinc oxide (ZnO) and titanium dioxide (TiO_2) were used as semiconductors at pilot plant scale(coating process) under natural sunlight.

The effect of sunlight and UV exposer results in lesser persistence of the molecule in environment and in turns, affects the bio-efficacy. In case of newer molecules having very short residual life , Da Silva et.al [6]; this problem gets more prominence, do there is an immense scope to improve the bio-efficacy of the molecule by stabilization during shelf life and field applications Shirley,et.al [7]. Inorganic UV stabilizers having unique advantages over the organic being non biogenic, they themselves are not biodegradable and therefore persist in the environment for longer time to save herbicide molecule ,rather by manipulation of the formulation system and so not interfere with herbicides own bio-efficacy. Use of inorganic stabilizers have been already been reported in different fields Klaus, Schutle. Yuzhuoli ; Sujata, Desai [8-9] like- plastic, paper, paints, woods, cosmetics and pharmaceutical industries.

However, its use as stabilizer in pesticide industry has hardly been reported. Accordingly attempts have been made in the present communiqué to report its stabilizing capability against ultra violet and sunlight degradation of organic herbicide Simazine and its formulations.

MATERIALS AND METHODS

Simazine technical sample (Batch No. # SMZ 098) was procured and prepared the simazine 70 WDG (Water dispersible granules formulation) by Balraj S. Parmar et.al, Chester L. Foy et.al and D.A. Knowles [10-12] , by using selected recipients like dispersing agent , wetting agent ,disintegrating agent , binder ,UV stabilizer and inert fillers ,formulation processed by using air jet milling to make homogenous powder and then prepared the sample by making dough with the help of required amount of water and prepared granules by using granulator ,like pan granulator ,basket extruders etc. Then dried in fluid bed dryer at heating temperature 54 ºC to the required moisture level for the study. Different concentrations (0.0, 0.5 and 1.0%) of titanium dioxide were prepared and used in this study. Simazine technical and its formulation were fortified with different concentrations of titanium dioxide as per experimental plan given below. The fortified samples were kept at 54°C for 14 days to study their heat stability. For UV stability samples were kept in ultraviolet cabinet at 254 and 360 nm wave length for controlled UV exposer and for sunlight stability the sample (amount of sample 20 g) were packed in white high density polyethylene (HDPE) and brown polyethylene ter phthalate (PET) bottle and kept in direct sunlight for 14 days. Degradation of active content of simazine technical and its formulation were studied by following the method (CIPAC ,Handbook, 1974)[13]. Samples analyzed by using gas-liquid chromatography technique by using Glass column of 1.8 m X 4 mm i.d. packed with 3 % carbowax 20 M on 80 to 100 mesh gas chrom Q. Condition the column at 240ºC for 24 h using carrier gas about 40 ml /min. Operating conditions was oven temperature 210ºC ± 5 ºC, injector temperature was 250 ºC, detector temperature was 250 ºC and carrier gas used was nitrogen or helium , 80 to 100 ml/min

Experimental design:

Sr. No	Details of studies carried out	Quantity of sample used in g	Concentration of titanium dioxide used	Duration of Study
1	Heat stability at 54°C	20 g sample is used for each study.	0.0, 0.5 and 1.0%	14 days
2	Ultraviolet stability in UV cabinet at 254 nm		0.0 and 1.0%	14 days
3	Ultraviolet stability in UV cabinet at 360 nm		0.0 and 1.0%	14 days
4	Sunlight stability in brown PET bottle		0.0 and 1.0%	14 days
5	Sunlight stability in white HDPE bottle		0.0 and 1.0%	14 days

RESULTS AND DISCUSSION

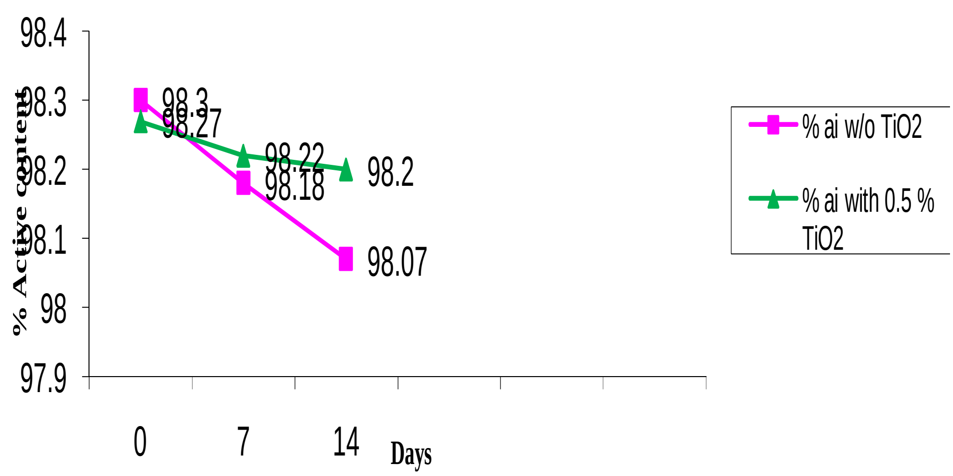
The results of various experiments (Sr. no 1 to 5) have been depicted in table 1-5 and Fig 1-12. At 54°C Simazine/formulation samples without having titanium dioxide degraded more in comparison to samples containing 0.5 to 1.0% titanium dioxide (Table 1, Fig 1-4). In respect of ultraviolet stability both at 254 and 360 nm addition of titanium dioxide proved to have stabilized the herbicide/formulation better in comparison to sample without having titanium dioxide (Table – 2, 3, Fig 5-8). Simazine technical and it's formulation is degrades more at 254 nm wavelength as compared to 360 nm wavelength. The addition of titanium dioxide at 1.0% proved to protect degradation of simazine/ formulation when exposed to sunlight in comparison to samples without titanium dioxide (Table 4, Fig 9-10). Simazine/formulation without titanium dioxide showed more degradation in comparison to samples having titanium dioxide at 1% concentration (Table – 5, Fig 11-12). Further, brown PET bottle was found to be a better container in comparison to white HDPE bottle.

Titanium dioxide present in sample is an excellent absorber of ultraviolet light, and a single, quarter-micron particle of TiO_2 will absorb in excess of 99% of all solar UV radiation that strikes it. The UV light energy is temporarily transformed into electronic energy in the form of an electronically excited TiO_2 particle, and then the vast majority of this energy gets quickly converted into heat energy. The heat energy then dissipates from the materials(Dr. Michael P. Diebold 2005) [14].

TiO_2 is an excellent UV light absorber. By removing the UV component of sunlight, the TiO_2 particles shield the molecules beneath them from direct degradation. This effectively limits direct degradation of simazine and it's formulations from UV light and sunlight.

When we packed samples in brown PET bottles we found that there is less degradation of Simazine content in technical and it's formulation as compared to the white HDPE bottles, because a chromatic (brown) color of glass or plastic containers. It is used principally to protect the contents of the container from exposure to light, as we know the chemicals which is affected by sunlight are always kept in amber colored glass bottles for e.g. Silver nitrate. Generally organic materials are light sensitive, to prevent their decomposition in light they are preserved mainly in amber colored bottles as this color filters the UV radiation and hence prevent their photo decomposition. PET is more resistant to heat as compares to HDPE.

Fig. No 1: Stability of Simazine technical at 54 °C for 14 days without and with 0.5 % TiO_2(Glass Bottles)



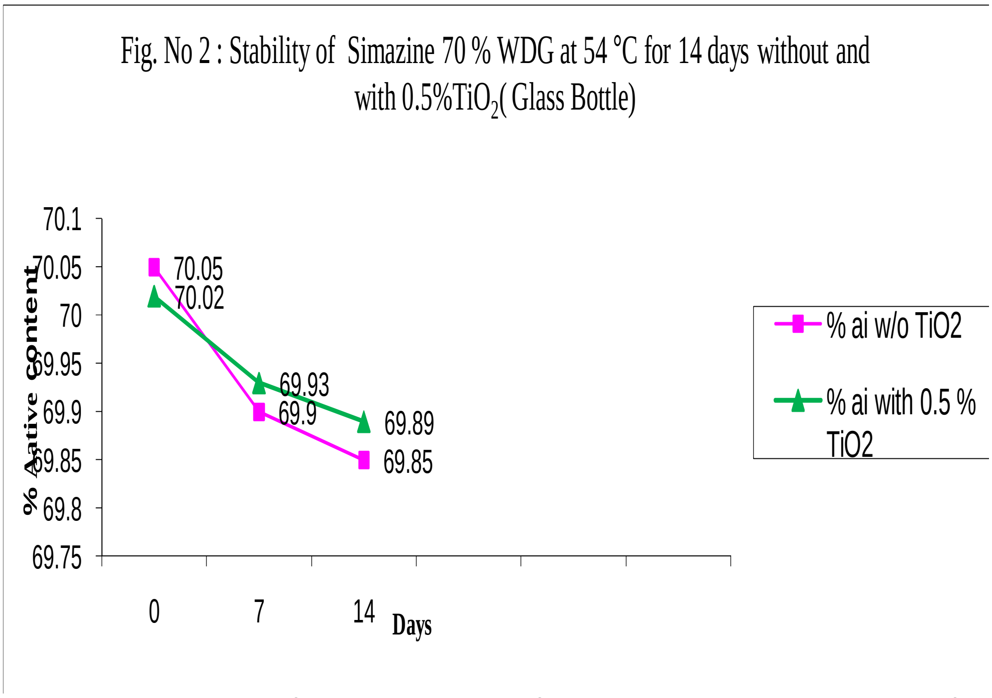


Table 1. UV stability of simazine technical and its formulation using 0.5 %and 1% TiO_2 at 54°C for 14 days.

Container used for the study: Glass bottles

Technical used for the study : Batch No. #SMZ 098

Sr.No.	Sample details	0day	7days	%difference	14 day	%difference
1	Technical without TiO_2	98.3	98.18	0.1221	98.07	0.2339
2	Technical with 0.5% TiO_2	98.27	98.22	0.051	98.2	0.0712
3	Technical with 1% TiO_2	98.26	98.24	0.0203	98.22	0.0407
4	70 % WDG without TiO_2	70.05	69.9	0.2141	69.85	0.2855
5	70 % WDG with 0.5% TiO_2	70.02	69.93	0.1285	69.89	0.1857
6	70 % WDG with 1% TiO_2	70.01	69.97	0.0571	69.94	0.0999

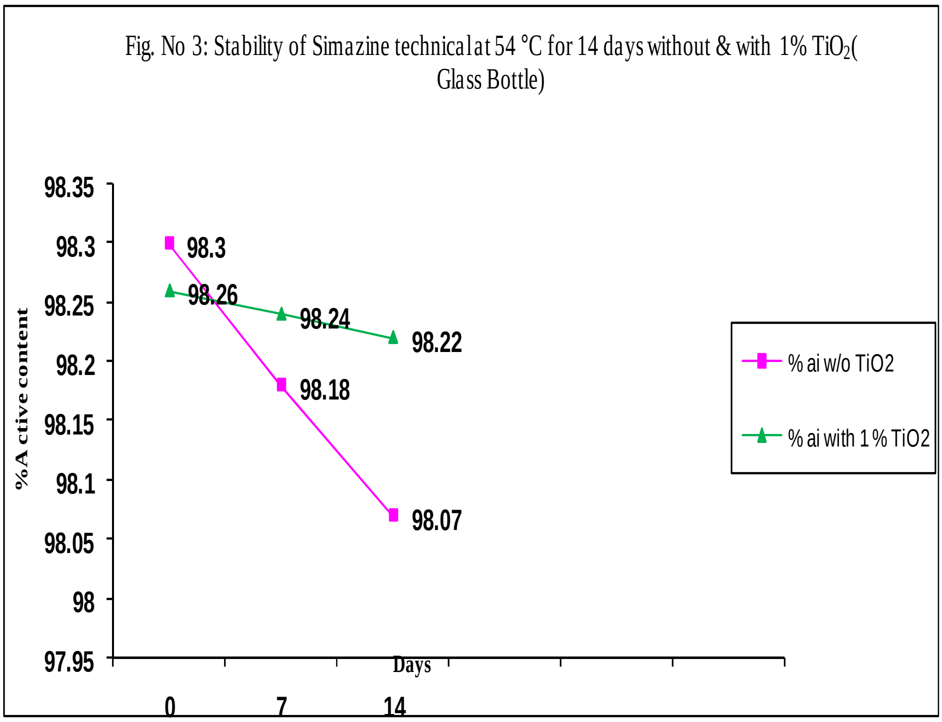


Fig. No 4 : Stability of Simazine 70 % WDG at 54 °C for 14 days without and with 1%TiO_2(Glass Bottle)

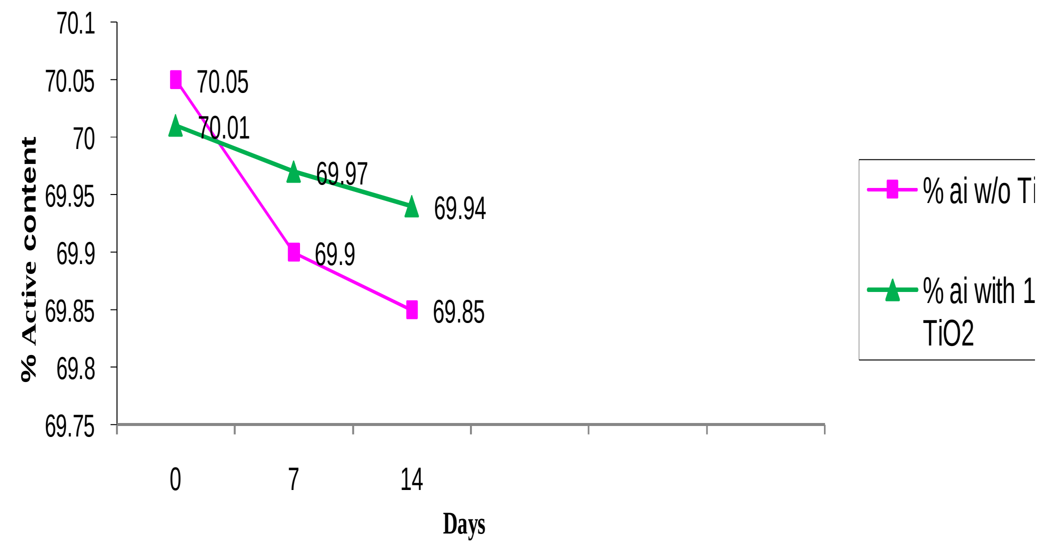


Fig. No 5 : Stability Simazine Technical in UV Cabinet at 254 nm for 14 days without and with 1 % TiO_2

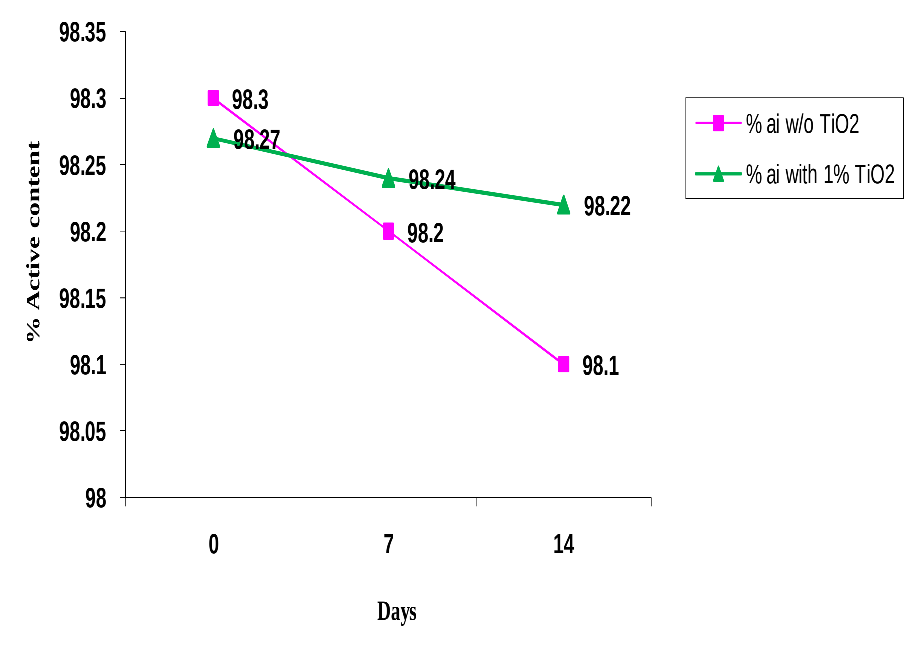


Table 2. UV stability of simazine technical and its formulation in UV cabinet at 254nm for 14 days.
Container used for the study: In glass bottles
Technical used for the study : Batch No. #SMZ 098

Sr.No.	Sample details	0day	7days	%difference	14 day	%difference
1	Technical without TiO_2	98.3	98.2	0.1017	98.1	0.2035
2	Technical with 1% TiO_2	98.27	98.24	0.0305	98.22	0.0509
3	70 % WDG without TiO_2	70.05	69.91	0.1998	69.83	0.3140
4	70 % WDG with 1% TiO_2	70.04	70.01	0.0428	69.98	0.0857

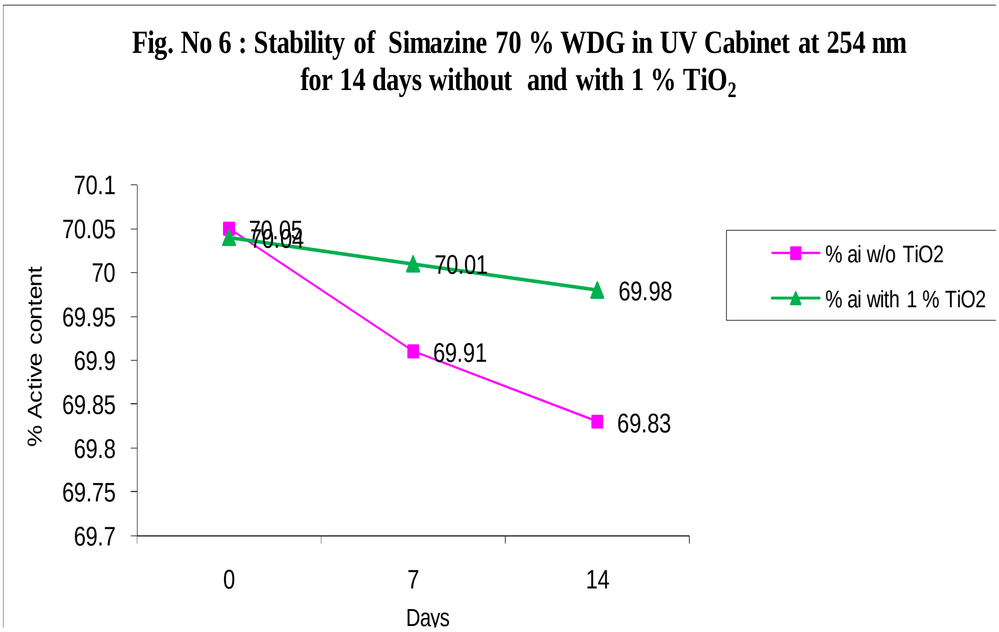


Table 3. UV stability of simazine technical and its formulation in UV cabinet at 360 nm for 14 days.
Container used for the study: In glass bottles
Technical used for the study: Batch No. #SMZ 098(Already exposed to 254 nm continued for 360 nm)

Sr.No.	Sample details	0day	7days	%difference	14 day	%difference
1	Technical without TiO_2	98.3	98.2	0.1017	98.12	0.1831
2	Technical with 1% TiO_2	98.27	98.25	0.0204	98.24	0.0305
3	70 % WDG without TiO_2	70.05	69.95	0.1427	69.85	0.2855
4	70 % WDG with 1% TiO_2	70.03	69.98	0.0714	69.95	0.1142

Table No. 4 Effect of sunlight on simazine and its formulation along with TiO_2.
Container used for the study: White HDPE bottles
Technical used for the study : Batch No. #SMZ 098

Sr.No.	Sample details	0day	7days	% difference	14 days	% difference
1	Technical without TiO_2	98.3	98.22	0.0814	98.17	0.1322
2	Technical with 1% TiO_2	98.28	98.25	0.0305	98.23	0.0509
3	70 % WDG without TiO_2	70.05	69.95	0.1428	69.87	0.2569
4	70 % WDG with 1% TiO_2	70.04	70	0.0571	69.98	0.0857

Fig. No 7: Stability SimazineTechnical in UV Cabinet at 360 nm for 14 days without and with 1 % TiO_2

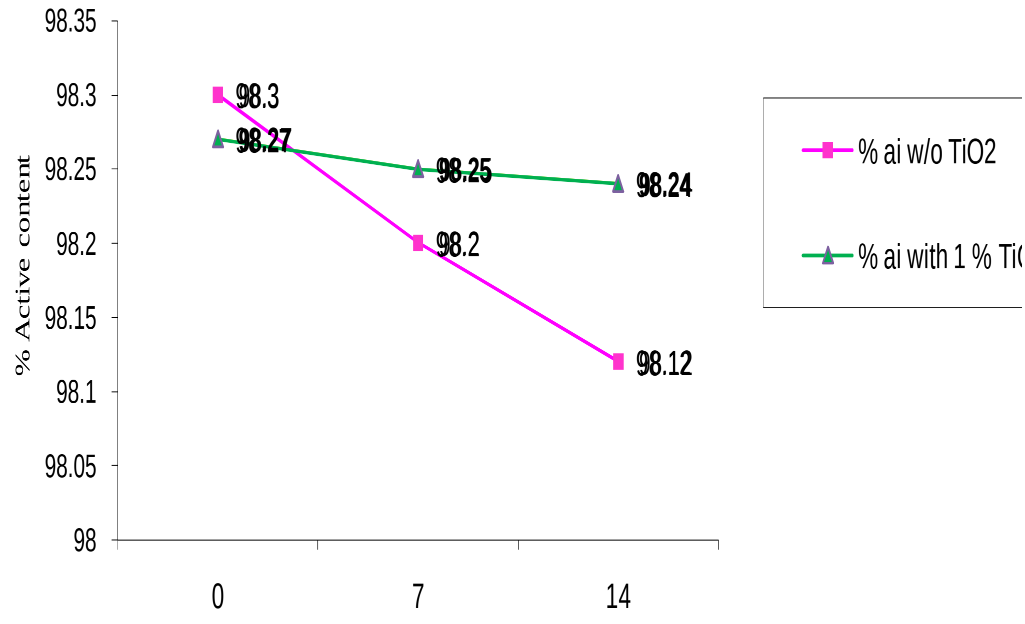
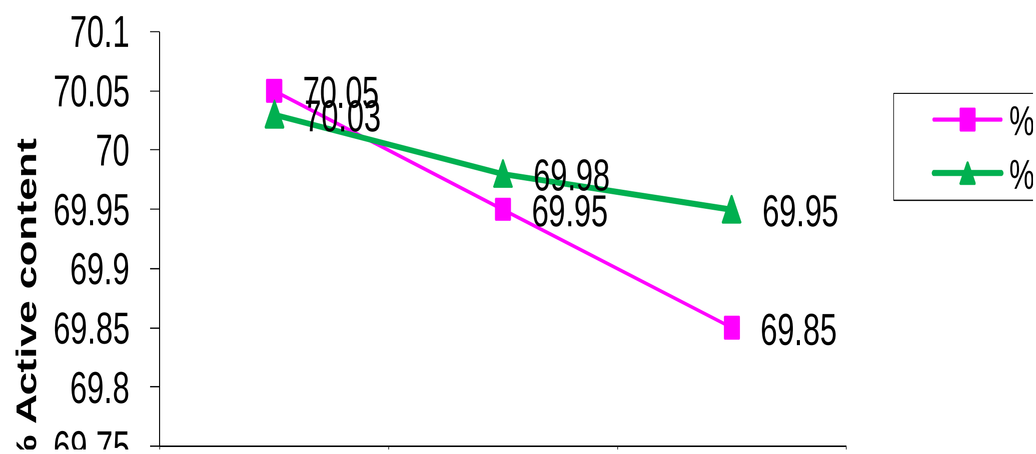
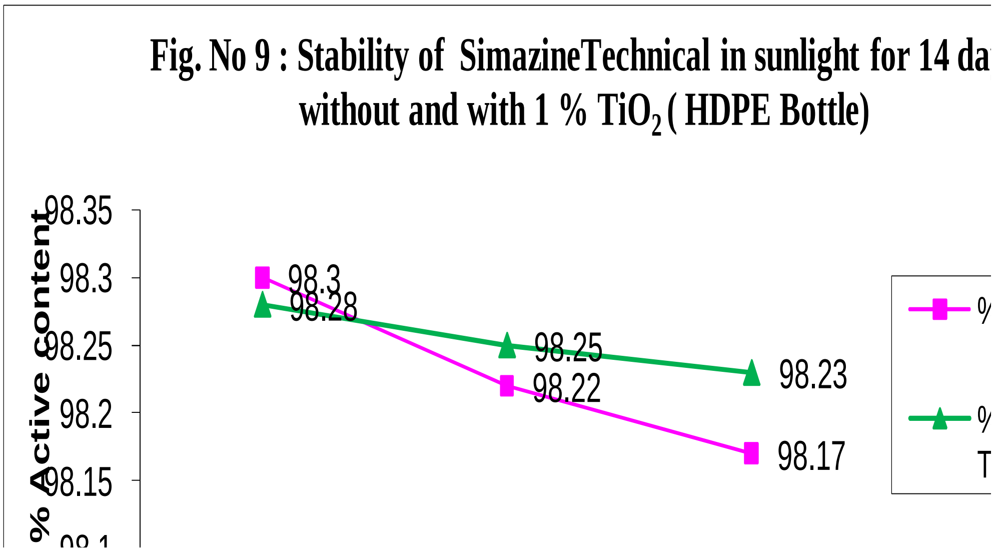


Fig. No 8 : Stability of Simazine 70 % WDG in UV Cabinet at for 14 days without and with 1 % TiO_2





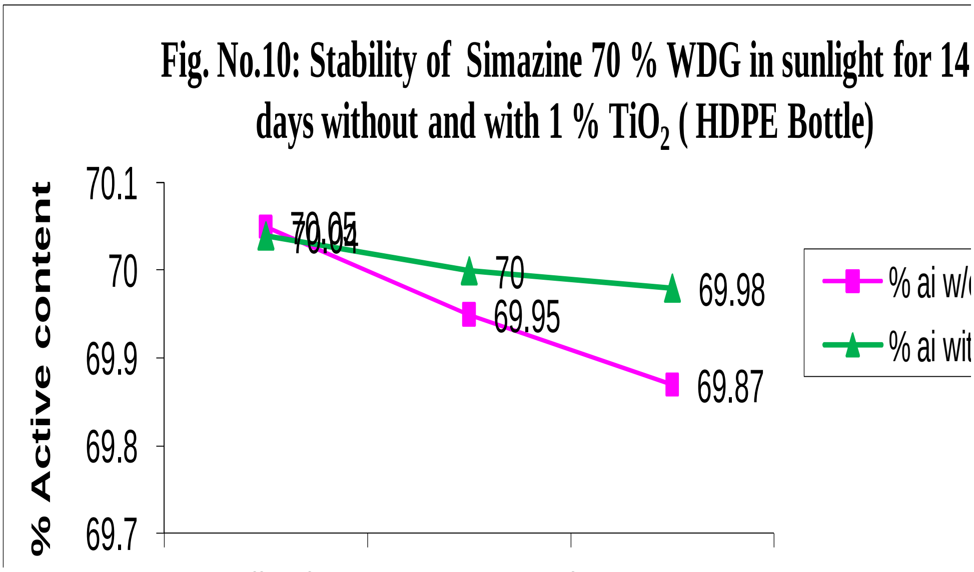


Table No.5 Effect of sunlight on simazine and its formulation along with TiO_2.

Container used for the study: Brown PET bottles

Technical used for the study : Batch No. # SMZ 098

Sr.No.	Sample details	0day	7 days	% difference	14 days	% difference
1	Technical without TiO2	98.3	98.23	0.0712	98.19	0.1119
2	Technical with 1% TiO2	98.3	98.28	0.0203	98.26	0.0407
3	70 % WDG without TiO2	70.05	69.97	0.1142	69.90	0.2141
4	70 % WDG with 1% TiO2	70.04	70.02	0.0286	70.01	0.0428

Fig. No 11: Stability of Simazine Technical in sunlight for 14 without and with 1 % TiO_2 (PET Bottle)

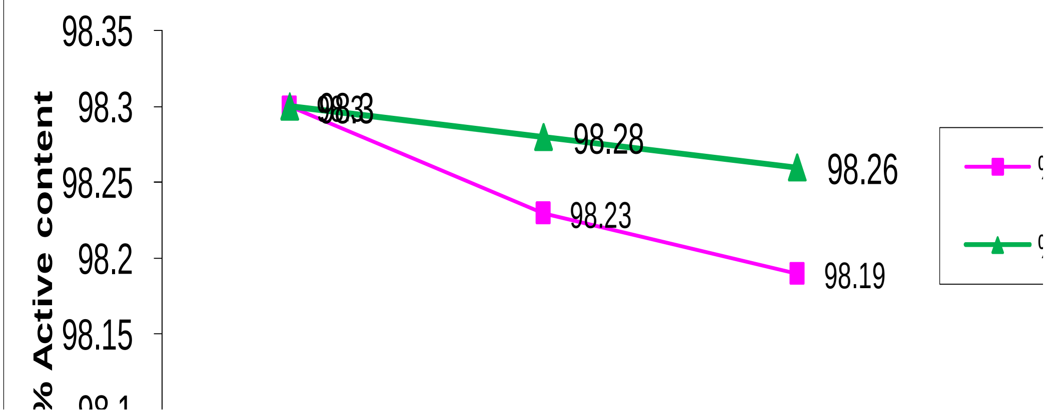
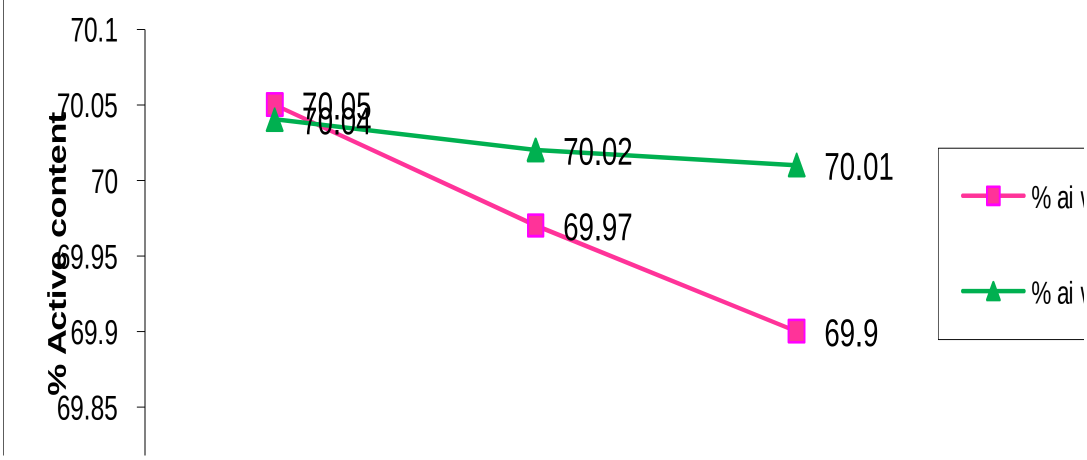


Fig.No 12 : Stability of Simazine 70 % WDG in sunlight for 14 days without and with 1 % TiO_2(PET Bottle)



CONCLUSION

Thus it is concluded that titanium dioxide even at lower concentration (0.5 to 1.0%) proved to be a good stabilizer at various adverse condition ,like heat stability at 54°C,exposure to various UV wavelengths i.e. 254 nm and 360 nm. for simazine (an organic herbicide) and its various formulations**.** The brown PET bottles shows good stabilization of simazine and its formulation against sunlight as compared to white HDPE bottles.

Acknowledgements
The authors are thankful to the Management of Shivaji University, Kolhapur and for extending all the necessary help provided for carrying out this study and their permission for publication.

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