https://doi.org/10.29321/MAJ.10.A03498

Deterioration in Pesticide Formulations during Storage

by

S RAMAN[1], N. S. VENKATARAMAN[2], V. RAVIKUMAR[3], and N. M. THYAGARAJAN[4]

Introduction: One of the recognised main requirements determining the efficacy of a pesticide formulation is its stability in storage. The different pesticides have to be procured well in advance and kept in sufficient stocks by dealers as well as by the farmers to meet the demands for plant protection operations during the proper time and season of the crops. There is no adequate information at present on the shelf life (stability) of the different pesticide formulations during storage apart from the claims of the manufacturing firms in respect of the stability of the basic technical materials used in the pesticide formulations. At the Pesticides Testing Laboratory, Coimbatore, deterioration was reported in active ingredients in some pesticide formulations (Thyagarajan and Venkataraman, 1967). Studies were continued in the Pesticides Testing Laboratory, Coimbatore on this aspect with some more pesticide formulations received for tests at the laboratory, adopting the usual methods of storage of pesticides purchased in the Agricultural Depots and the results are presented below.

Materials and Methods: Studies were undertaken with samples of insecticides *viz* Endrin 2% granules, Carbaryl 10%, Carbaryl 50% W.P., Carbaryl 85% W.P., Dimethoate 30% E.C., Malathion 4% dust and Malathion 50% E.C., and with an organo-mercurial dry seed dressing formulation. The samples for the examination were drawn and kept in air tight bottles in a place free from excessive humidity and well protected from contact with moisture and direct sunlight. Samples in the bottles were tested periodically for the active ingredient content of the pesticide concerned. The content of Endrin 2% granules was estimated by (Sodium isopropylate) total organic chlorine method, carbaryl in Carbaryl 10%, 50% and 85% formulations was determined by alkaline hydrolysis method. Dimethoate in the 30% E.C., formulation, by hydrolysis as methylamine, Malathion by iodometric method and Mercury in the seed dressing formulation by the thiocyanate method.

The percent active ingredient lost if any during the interval between the estimations done initially and at the time of examination during the storage for the individual pesticides was calculated. The active ingredient for which the samples were analysed, the period of interval between the estimations and the percent lost during that interval were calculated and are presented in the Table.

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1 & 2. Assistants in Chemistry, 3. Assistant Agricuitural Chemist, 4. Agricultural Chemist and Associate Professor of Soil Science.

TABLE. *Showing the pesticide, period stored, active ingredient percentage and loss of active ingredient if any during storage*

Name of sample	Period	Active ingredient % by wt.	Fall in active ingredient	% active ingredien lost with respect o the initial value
I. Endrin 2% granules				
	Initial	2.04	—	—
	3 months	1.95	0.09	4.41
	9 months	1.91	0.13	6.37
	17 months	1.88	0.16	7.84
	21 months	1.72	0.32	5.68
	29 months	1.58	0.46	2.55
II. Carbaryl 10% dust				
	Initial	10.64	—	—
	6 months	10.38	0.26	2 44
	21 months	10.19	0.45	4.23
III. Carbaryl 50% W.P.				
	Initial	50.10	—	—
	6 months	49.34	0.76	1.52
	24 months	48.01	2.09	4.17
IV. Carbaryl 85% W.P.				
	Initial	83.54	—	—
	6 months	83.45	0.09	0.11
	9 months	83.37	0.17	0.20
	1 year	83.28	0.26	0.31
	2 years	83.26	0.28	0.33
V. Carbaryl Technical				
	Initial	97.97	—	—
	21 months	97.92	0.05	00.5
VI. Dimethoate 30% (W/V) E C. (Rogor 40)				
	Initial	31.00	—	—
	6 months	30.35	0.65	2.10
	12 months	30.15	0.85	2.74
VII. Malathion 4% dust				
	Initial	4.06	—	—
	5 months	3.55	0.51	12.56
	11 months	3.09	0.97	23.90
	16 months	2.38	1.68	41.38
VIII. Malathion 50% E.C.				
	Initial	50.14	—	—
	4 months	46 89	3.25	6.48
	12 months	45.16	4.98	9.93
	24 months	43.14	7.00	13.96
IX. Shell seed dresser 1% Mercury				
	Initial	1.003	—	—
	3 months	0.863	0.140	13.96
	8 months	0.824	0.179	17.85
	17 months	0.702	0.301	30.01

Results and Discussion: There is a striking deterioration in the content of active ingredient in Endrin 2% granules, Malathion 4% dust, Malathion 50% E.C., and in the organo-mercurial seed dresser, as seen from the Table, the maximum deterioration having been indicated in Malathion dust and in the Mercury formulations, with a fall of 41.38% and 30.01% respectively during the period of 16 and 17 months respectively. The sample of Malathion dust deteriorated very considerably than Malathion E. C. Technical grade malathion is said to be stable for an indefinite period of time if stored under proper conditions, and the technical and liquid formulations may gel if they are placed in contact with iron and tin plate for a long period (Cyanamid India Ltd., Publication). Masao Yamauschi *et al.* (1959) have reported that moisture had no effect on the decomposition of Malathion in dust compositions but emulsions were decomposed in proportion to moisture. Hiroshi-Takehara (1965) has reported based on studies about stability of phenyl mercuric acetate dust formulations that although there was no remarkable change in total mercury content in the dust formulation, the concentration of phenyl mercury acetate decreased to 81.2 and 84.1% of the original amount when stored with talcum and calcium carborate as diluents respectively for one year at 40°C Phenyl mercuric acetate was relatively stable when Zecklite (purified Kaolin clay) or clay was used as diluent. Frear and Dills (1967) have attributed moisture, pH and temperature as some of the factors responsible for reduction of mercuric salts to metallic mercury and consequent volatisation as vapours. The deterioration was not so marked in the case of Dimethoate 30% E.C., Carbaryl 10% dust and Carbaryl 50% W.P. when compared with Endrin, Malathion and Mercury in the present study and practically no deterioration has occurred in Carbaryl 85% W.P. The maximum fall in active ingredient noted in these formulations was 2 74% in Dimethoate 30% E C., during one year, 4 23% in Carbaryl 10% dust in 21 months, 4 17% in Carbaryl 50% W.P. during a period of 24 months and 0.33% in Carbaryl 85% W.P. during the same period. A sample of Carbaryl technical when similarly stored and analysed has not shown any deterioration up to 21 months. This is in conformity with the claim of the firm to the effect that Carbaryl is stable under prolonged storage (Union Carbide Corporation, New York, Publication, 1962).

From the data in the Table, it is seen that the extent of deterioration of the same pesticide in different formulations varies inversely with the concentration in the formulation. Thus the dust and granular formulations with low concentrations of the active materials (*viz.* Endrin 2% granules, Mercury 1%, Malathion 4% and Carbaryl 10%) have deteriorated at a faster rate than in the case of emulsifiable concentrates or wettable powder (Malathion E.C., and Carbaryl W.P.) with a high content of the same pesticide. This phenomenon may be attributed to the fact that eventhough

the diluents were chemically inert, they had certain physical handicaps such as absorption of moisture agglomeration of particles *etc.* during the storage period which led to the deterioration of the product.

Conclusion: The study has revealed that the formulations with low concentrations of active ingredients such as organo-mercurial seed dresser 1%, Malathion 4% and Endrin 2% granules deteriorated rapidly in storage. The deterioration in Malathion 50% E.C., was only at a lesser extent. The formulations of Dimethoate 30% E C., Carbaryl 10% dust and Carbaryl 50% W.P. were relatively more stable.

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* Original not seen.