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Decomposition of the Active Ingredient of Pesticides During Storage

by

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Introduction: The effect of exposure of pesticides and formulated products to atmospheric conditions, particularly to high summer temperatures is considerable. At Rothamsted, Burt and Ward (1955) have explained the rapid volatalisation of D. D. T. in summer as due to high temperature. Cases of adverse effect of high temperature favouring the inactive isomer of organo-phosphorus compounds which are isomeric mixtures of thions or thionol are reported from U. S. A. Materials are imported out of season or delayed in transit. Importers get surplus stocks and dump the stocks lest the users preference should change in the coming season or hoard the pesticides. All these entail storage of such pesticides for considerable time. Wallace and Martin (1954) reported such lapse of considerable time between the date of manufacture and the date of use in the field for crop protection chemicals in U. K. and Commonwealth countries. In India, large stocks of pesticides are held by several agricultural depots in the different States and a variety of pesticides are stored for long periods. Information on the keeping quality is essential for advice on the purchase and storage of pesticides by Government and ryots. The Pesticide Testing Laboratory at Coimbatore took up investigations on this aspect, adopting the usual methods of storage of the pesticides handled in the agricultural depots and the results are presented.

Material and Methods: In the agricultural depots the pesticides are stored, usually kept in covered containers in a place free from excessive humidity, avoiding direct sunlight and so, generally well protected from wind, rain and sun. These conditions were particularly observed in the laboratory and samples were drawn in air-tight bottles and kept in a place free from excessive humidity, protected from contact with water and direct sunlight. Studies were carried out with samples of fungicides Dithane (Zinc ethylene bis-dithiocarbamate) 6 per cent dust, Zineb (Zinc ethylene bis-dithiocarbamate) 65 per cent wettable powder, Dithane M. 45 (Zinc and Manganese complexed ethylene bis-dithiocarbamate) wettable powder, Cop-chloran 6 per cent dust, Cop-chloran 40 per cent wettable powder, Coppesan wettable powder, Cop-chloran 50 per cent concentrate (formulations containing copper oxy-chloride

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corresponding to 6 per cent, 40 per cent, 45·5 per cent and 50 per cent metallic copper respectively and insecticides Aldrex (Aldrin-chlorinated hydrocarbon) 5 per cent dust, Endrin 20 per cent E. C. (chlorinated hydrocarbon) and Paramar 50 E. C. (Parathion 50 per cent E. C.). Samples were drawn periodically from the bottles in which they were stored and the active ingredient determined. The pesticides were analysed for the respective active ingredient by the methods given below: Dithane 6 per cent dust, Zineb 65 per cent wettable powder and Dithane M. 45 were analysed by the method given out by Clarke *et al.* (1951). The copper fungicides were analysed as per the Indian Standard Specification 1506/1960 and 1507/1960 respectively for dusts and wettable compositions. Aldrin 5 per cent dust and Endrin 20 per cent E. C. were analysed for Aldrin and Endrin content respectively by the methods given in the Indian Standard Specifications for Aldrin dusting powders No. I. S. 1308/1958 and for Endrin E. C. No. I. S. 1310/1958. The Parathion content in the Paramar-50 sample was estimated by the method described in Indian Standard Specification for Parathion E. C. No. I. S. 2129/1962.

The per cent active ingredient lost during the interval between two estimation for the individual pesticides was calculated. The active ingredient for which the samples were analysed, the period of interval between two estimations and the per cent active ingredient lost during that interval are presented in the Table.

Showing the pesticides analysed during storage, period for which stored, content of active ingredient and loss of active ingredient during storage.

Name of sample	Period	Active ingredient Per cent by weight	Fall in active ingredient	Per cent active ingredient lost with respect to the initial content of the active ingredient
FUNGICIDES:				
Dithane 6% dust	Initial	5·064	...	...
	17 months	4·261	0·803	15·86
	22 months	4·214	0·850	16·78
	26 months	4·103	0·961	18·98
	30 months	4·075	0·089	19·53
Zineb 65% Wettable Powder	Initial	57·14	...	...
	15 months	55·90	1·25	2·19
	17 months	53·92	3·22	5·64

Name of sample	Period	Active ingredient per cent by weight	Fall in active ingredient	Per cent active ingredient lost with respect to the initial content of the active ingredient
Dithane M–45	Initial	61·35	...	...
	3 months	48·35	12·59	20·51
	6 months	46·09	15·26	24·86
	9 months	45·88	15·47	25·22
Cop-chloran 6% dust	Initial	6·879	...	...
	21 months	6·873	0·006	0·087
	27 months	6·676	0·203	2·95
Cop-chloran 40% W. P.	Initial	38·33	...	...
	21 months	38·30	0·03	0·078
	27 months	38·24	0·09	0·23
Cop-chloran 50% concentrate	Initial	49·84	...	...
	21 months	49·61	0·23	0·46
	27 months	49·45	0·39	0·78
Coppesan 45·5% Wettable Powder	Initial	49·84	...	...
	20 months	45·44	0·31	0·68
	27 months	45·36	0·39	0·85
INSECTICIDES:				
Aldrin 5% dust	Initial	4·49	...	...
	15 months	4·46	0·03	0·67
	18 months	4·46	0·07	1·56
	22 months	4·34	0·15	3·34
Endrin 20% E. C.	Initial	19·13	...	...
	15 months	18·78	0·35	1·1[illegible]
	18 months	18·58	0·55	2·8[illegible]
	22 months	17·62	1·51	7·8[illegible]
Parathion 50% E. C.	Initial	48·95	...	...
	9 months	48·43	0·52	1·0[illegible]
	12 months	48·31	0·64	1·31
	18 months	48·04	0·91	1·8[illegible]
	24 months	47·87	0·98	2·00

Results and Discussion: Dithane E-45 showed a sharp decline for the dithiocarbamation for which the fungicide was analysed. A reduction of 12·59 per cent in three months was noted. Dithane 6 per cent dust and Zineb

65 per cent wettable powder showed a decline in the active ingredient of 0·80 per cent in 17 months and 1·24 per cent in 15 months respectively. The copper compounds generally showed a loss of less than one per cent even after 27 months storage.

Aldrin dust and Endrin E. C. showed a decline of 1·56 per cent and 2·9 per cent respectively of the active ingredient based on the nominal value in 18 months. Parathion 50 per cent E. C. registered a decline of 0·91 per cent during the course of 18 months, which corresponds to a loss of just 1·86 per cent with respect to the nominal value during the period.

The rapid decomposition in Dithane M-45 was mainly due to the Manganese compound being not stable and to an extent due to the incompatibility of Manganese and Zinc ethylene bis-dithiocarbamates. The active ingredient lost in the case of Zineb 65 per cent Wettable Powder was much less compared to the 6 per cent dust. The data also revealed that considerable decline in the active ingredient would occur in about five years in the case of dilute formulations of Zineb and the active substance is not lost so rapidly in the concentrated formulations.

Eventhough the diluents were chemically inert they had certain physical handicap such as absorption of moisture, bigger particle size *etc.*, which led to deterioration of the product during the storage period.

The method of determination of Parathion was based on the estimation of nitro group. Since this group is comparatively stable, the loss was not representative of the loss in the active group C_2H_5-OSP- which exists in an equilibrium mixture of thiono and the thionol forms. Aldrin on account of its more stable molecular configuration showed a less steep slope than Endrin. The data showed that Aldrin should keep well for about six years without much decomposition and Endrin as more unstable decomposing at a faster rate than Aldrin.

Conclusion: The fungicide Dithane M–45 has to be used within a few months of its manufacture and formulation. Zineb when stored in a diluted formulation deteriorates more rapidly than when stored as a concentrated formulation. Zineb 65 per cent wettable powder would keep well for a longer period than 6 per cent dust which would keep well only up to five years. Lowering the strength of Zineb by addition of diluents hastens decomposition during storage. In the case of formulations of copper-oxy-chloride, the actual decomposition, as indicated by the copper content is negligible but this is not necessarily indicative of their fungicidal efficacy.

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