

COMPARATIVE STUDY OF PHOSPHINE GENERATING SUBSTANCES AVAILABLE IN PAKISTAN

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Phosphine generating formulations which are being used in Pakistan have been evaluated for their performance by analysis for aluminium phosphide content, presence of ammonium carbamate, urea, sodium chloride, petroleum ether soluble substances, the rate of evolution of hydrogen phosphide as a function of time when left in the open, minimum time of phosphine release after exposure and fire hazard on adding one ml water per tablet.

The formulation can be categorised into (1) those containing ammonium carbamate and (2) those containing urea and sodium chloride. The presence of carbamate is effective in protecting the tablets from spontaneous ignition on adding water. On the other hand the reaction with water is violent in the case of sodium chloride and urea containing tablets since after 21-25 minutes the phosphine evolved catches fire.

INTRODUCTION

Fumigants most frequently used in the protection of stored grains are methyl bromide, hydrocyanic acid, ethylene dibromide, and chloride, carbon tetrachloride and hydrogen phosphide [1,2]. However, most of them are candidates in the list of potentially toxic chemicals. Phosphine generating substances have so far been shown to be safe in application and do not pose many problems in storage.

Phosphine generating substances are coming into increasing use in Pakistan for grain fumigation. The import of these substances has gone up from 2.4 tons/annum to 110 tonnes/annum during the last ten years. The upward trend is because of the export requirements of an agricultural product, namely rice, and also because of large silos being constructed for the storage of wheat in which the country has now attained self sufficiency.

With the increase in use of fumigants and the absence of manufacturing capability in the country, a number of products are being imported from various countries. This paper presents analytical data and test results on seven of the imported tablets/formulations.

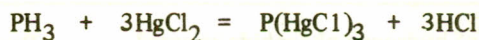
- | | |
|------------------------------|--|
| (A) Phostoxin-R (Degesch) | (B) Detia Gas Ex-T |
| (C) Fumitoxin | (D) Phostoxin Prepac |
| (E) Gastoxin Delecia (India) | (F) Gastoxin Delecia
(East Germany) |
| | (G) Detia Gas Ex-B
(Bags) |

The requirements for phosphine generating aluminium phosphide tablets as per the environmental condition in Pakistan are:

- (i) The gas should not release instantaneously
- (ii) It should be possible to dispose of the residue
- (iii) There should be no fire hazard on reaction with water.

EXPERIMENTAL

The analysis of hydrogen phosphide was carried out by the acid hydrolysis of aluminium phosphide [4,6]. This process released hydrogen phosphide, which is absorbed in a 1.5% solution of mercuric chloride. The acid formed



during the reaction is titrated to give the amount of phosphine released.

The ignition test was performed by placing 20 tablets and adding 20 ml water in one litre beaker in which a thermometer was placed. The beaker was covered with a watch glass and temperature was noted at 2 min interval.

The experiments were conducted in Nov. and Dec. 1979. Temperature and RH were between 25-26°C and 53-56% respectively.

The amount of ammonium carbamate was determined by analysis of its decomposition products, viz. carbon dioxide and ammonia. Analysis of urea, common salt, petroleum ether soluble waxes and stearates were carried

out by the reported method [3].

The rate of the release of hydrogen phosphide was found by keeping a known amount of samples separately in Petri dishes and placing them in the open. Each sample was analysed hourly for six hours and then at 24 hr. intervals upto 96 hr. The results are shown in Table 2.

The release of hydrogen phosphide when the aluminium phosphide tablets are exposed to open air was found by keeping them in a two neck round bottomed flask. Its outlet was connected to a mercuric chloride absorption bottle through a delivery tube. Suction was applied at the absorption bottle end and the time for appearance of turbidity was noted in the mercuric chloride solution.

RESULTS AND DISCUSSION

It may be seen from Table 1 that A, B, C and D contained aluminium phosphide, ammonium carbamate and petroleum ether soluble substances while E, F and G had aluminium phosphide, common salt, a small percentage of urea and petroleum ether soluble substances.

Aluminium phosphide present in different aluminium phosphide formulations is shown below:

Formulation	(A)	(B)	(C)	(D)	(E)	(F)	(G)
Found (%)	61.05	59.90	56.70	50.23	57.23	52.49	52.32
Claimed (%)	56-57	56-57	56-58	56.00	56-58	56-58	56.0

It would be seen from the above Tables that there is a variation between the aluminium phosphide claimed and what is actually present.

The values obtained from Table 2 indicate the amount of hydrogen phosphide released after a definite time interval. It may be seen that during 6, 24 and 96 hr the release were as follows:

	Amount of hydrogen phosphide released after			Residue after 96 hours (%)
	6 hours (%)	24 hours (%)	96 hours (%)	
A.	10.8	29.0	34.1	1.7
B.	16.23	28.67	32.66	2.34
C.	10.97	29.3	31.83	1.53
D.	12.95	25.05	27.65	1.9
E.	13.68	25.92	30.97	2.75
F.	11.75	22.6	28.05	2.73
G.	9.49	22.6	29.08	.7

The maximum evolution of hydrogen phosphide within 96 hr was found more in A, B and C as compared with D, E, F, and G.

A graphic presentation (Fig. 1-2) of the above results indicates that the maximum release of hydrogen phosphide was between 6-24 hr and thereafter it slowed down. The fumigation is usually carried out in closed rooms, godowns, or vaults for 24 hr and hence it would add to the efficiency of the formulation if maximum gas is evolved within 24 hr and also if the residue is largely free of hydrogen phosphide. The efficiency of release is as follows:

Formulation	Time Intervals (Hours)		
	6	24	96
	%	%	%
A	30.0	81.0	95.0
B	46.0	81.9	93.0
C	33.88	87.81	95.41
D	43.82	84.77	93.57
E	40.0	76.8	91.8
F	38.0	73.0	91.0
G	30.83	73.62	94.47

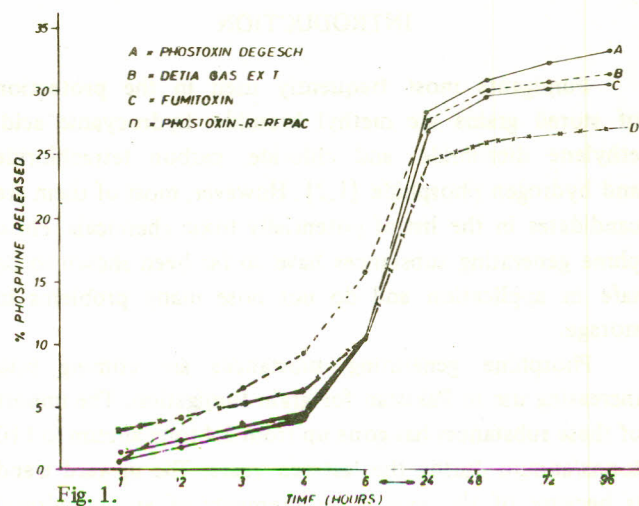


Fig. 1.

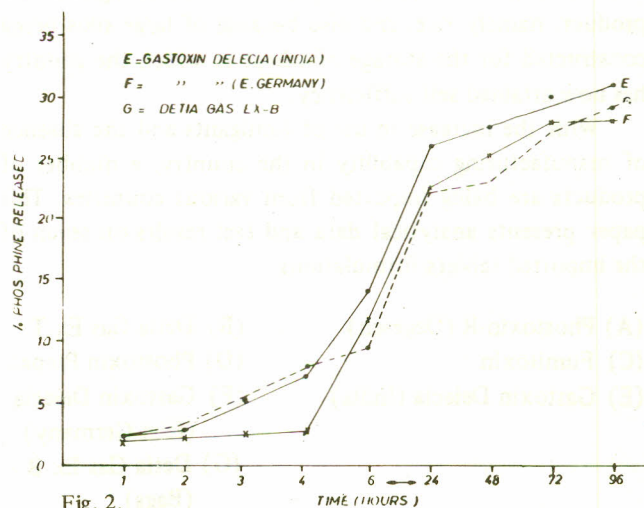


Fig. 2.

As stated earlier it is important for a fumigant tablet or system that it should not release the toxicant immediately but should do so very slowly in the initial stage. It was found (Table 1) that the decomposition of aluminium phosphide when exposed to air was quicker for A, B, C, D and G than for E, F, but quantitative release of hydrogen phosphide in one hour was more from D, E, F and G than from A, B and C (Table 2)

Release of hydrogen phosphide in one hour

	(A)	(B)	(C)	(D)	(E)	(F)	(G)
hydrogen phosphide in one hour	1.3	0.51	1.04	3.17	2.42	2.08	2.08

Fumigation tablets, as pointed out earlier, are required to take care of the fire hazard due to instantaneous release of the gas. Since phosphine catches fire instantaneously, it is pertinent to note that the tablets should be carefully prepared to minimise the risk of fire. From Table 4 it is noted that the maximum temperature of 90°C was recorded for A which was reached in 80 min. 65°C for B and C in 45 and 14 min respectively, 108°C for D in 18 min, 50°C for E and F in 21 to 25 min and 95°C for G in 30 min. The temperature rose quickly from 40 to 50°C within 21-25 min for E and F while at the latter temperature both

Table 1. Analytical data of phosphine generating substances available in Pakistan.

	Phostoxin Degesch (tablets) Fed. Rep. of Germany (A)	Detia gas Ex-T (tablets) Fed. Rep. of Germany (B)	Fumitoxin (tablets) China (C)	Phostoxin R-Repac pellets) Fed. Rep. of Germany (D)	Gastoxin Delecia (tablets) India (E)	Gastoxin Delecia (tablets) East Germany (F)	Detia gas Ex-B (powder) Fed. Rep. of Germany (G)
1. Aluminium phosphide (%)	61.05	59.70	56.90	50.23	57.51	52.49	52.32
2. Hydrogen phosphide (%)	35.80	35.01	33.36	29.55	33.72	30.78	30.78
3. Ammonium carbamate (%)	18.4	21.8	19.92	16.50	NIL	NIL	NIL
4. Urea (%)	NIL	NIL	NIL	NIL	3.3	2.78	6.0
5. Sodium chloride (%)	NIL	NIL	NIL	NIL	18.49	17.43	17.23
6. Pet. ether soluble substances (%)	5.96	4.42	5.4	3.5	9.75	10.13	3.5
7. Inert material/fillers	14.59	4.78	17.78	29.77	10.95	17.17	20.95
8. Minimum time of PH ₃ release	1-2 min.	2.5 min.	30 sec	already releasing	3-4 min.	3-4 min.	already releasing
9a. Weight of residue after 96 hr	Decreased 11.37% in 24 hr increased 0.178% after 96 hr	Decreased 10.5% in 24 hr; increased 1.8% after 96 hr	Decreased 10.1% in 24 hr. increased <1% after 96 hr.	Decreased 10.4% in 24 hr increased <1% after 96 hr.	Increased 10.9% in 24 hr and 22.7 % in 96 hr	Increased 10.7% in 24 hr and 23.3% in 96 hr	Increased 10.5% in 24 hr and 16.1% in 96 hr
b. Residue analysis: ALP: PH ₃	2.89% 1.70%	3.99% 2.34%	2.61% 1.53%	3.23% 1.90%	4.69% 2.75%	4.65% 2.73%	2.89% 1.70%
10. Fire hazards - reaction on addition of 20 ml water/20 tablets	No fire, no explosion, max. temp. 90°C	No fire, no explosion, max. temp. 65°C	No fire, no explosion, max. temp. 65°C	No fire, no explosion max. temp. 108°C	cought fire after 21-25 min .temp. 50°C	caught fire after 21-25 min temp. 50°C	No fire, no explosion, max. temp. 95°C

Table 2. Hydrogen phosphine found, released and efficiency of release with time.

Time in hours	Phostoxin Degesch (A)			Detia Gas Ex-T (B)			Fumitoxin (C)			Phostoxin-R-Repac (D)			Gastoxin Delecia India (E)			Gastoxin Delecia East Germany (F)			Detia Gas Ex-B (G)		
	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency	PH ₃ found	PH ₃ released	PH ₃ released efficiency
0	35.8	0.0	0.0	35.0	0.0	0.0	33.36	0.0	0.0	29.55	0.0	0.0	33.72	0.0	0.0	30.78	0.0	0.0	30.78	0.0	0.0
1	34.5	1.3	3.6	34.49	0.51	1.4	32.32	1.04	3.11	26.38	3.17	10.72	31.30	2.42	7.0	28.7	2.08	6.7	28.75	2.08	6.75
2	33.5	2.3	6.4	30.74	4.26	12.0	31.40	1.96	5.87	25.5	4.05	13.7	30.92	2.8	8.0	28.46	2.32	7.5	28.46	2.32	7.53
3	32.0	3.8	10.6	28.47	6.53	18.6	29.8	3.56	10.43	24.1	5.45	18.44	28.49	5.23	15.5	28.2	2.5	8.3	28.10	2.68	8.7
4	31.7	4.1	11.4	25.5	9.5	27.1	29.09	4.27	12.78	23.3	6.25	21.15	26.62	7.1	21.0	27.99	2.79	9.0	27.99	2.79	9.06
5	-	-	-	22.66	12.34	35.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	25.0	10.8	30.0	18.77	16.23	46.0	22.39	10.97	33.88	16.6	12.95	43.82	20.04	13.68	40.0	19.03	11.75	38.0	21.29	9.49	30.83
24	6.8	29.0	81.0	6.33	28.67	81.9	4.06	29.3	87.81	4.5	25.05	84.77	9.8	25.92	76.8	8.18	22.6	73.0	8.18	22.6	73.62
48	4.25	31.55	88.0	2.68	32.32	92.0	2.88	30.48	91.36	2.9	26.65	90.18	6.7	27.02	80.0	5.55	25.23	81.0	7.8	22.98	74.65
72	2.7	33.1	92.0	2.4	32.5	92.9	2.0	31.3	93.9	2.3	27.25	92.21	3.8	29.91	88.7	2.8	27.98	90.0	3.4	27.38	88.95
96	1.7	34.1	95.0	2.34	32.66	93.0	1.53	31.83	95.41	1.9	27.65	93.57	2.75	30.97	91.8	2.73	28.95	91.0	1.7	29.08	94.47

Table 3. Rate of decomposition of active ingredient (AIP)

Time in	Phostoxin Degesch (A)			Detia Gas Ex-T (B)			Fumitoxin (C)			Phostoxin-R-Repac (D)			Gastoxin Delecia India (E)			Gastoxin Delecia East Germany (F)			Detia Gas Ex-B (G)		
	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed	AIP found %	AIP decomposed %	% efficiency of AIP decomposed
zero	61.05	0.0	0.0	59.70	0.0	0.0	56.9	0.0	0.0	50.23	0.0	0.0	57.51	0.0	0.0	52.49	0.0	0.0	52.32	0.0	0.0
1	58.83	2.21	3.6	58.80	0.9	1.4	55.13	1.77	3.11	48.85	5.38	10.71	53.38	4.13	7.0	48.94	3.45	6.7	48.79	3.53	6.74
2	57.13	3.92	6.4	52.4	7.3	12.0	53.56	3.34	5.86	43.35	6.88	13.69	52.73	4.78	8.0	48.53	3.85	7.5	48.38	3.94	7.53
3	54.57	6.48	10.6	48.54	11.16	18.6	50.83	6.07	10.43	41.00	9.23	18.37	48.31	9.2	15.5	48.1	4.4	8.3	47.77	4.55	8.7
4	54.06	6.99	11.4	43.5	16.2	27.1	49.62	7.28	12.78	39.61	10.62	21.14	45.39	12.1	21.0	47.73	4.76	9.0	47.58	4.74	9.06
5	-	-	-	38.64	21.06	35.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	42.5	18.55	30.0	32.0	27.7	46.0	38.1	18.7	32.9	31.5	24.6	21.8	34.06	23.45	40.0	32.35	20.14	38.0	36.1	16.1	30.8
24	11.59	49.45	81.0	10.79	48.91	81.9	6.92	49.98	87.81	7.65	42.58	84.77	13.30	44.2	76.8	13.95	38.44	73.0	13.9	38.42	73.42
48	7.24	53.8	88.0	4.56	54.44	92.0	4.92	51.98	91.36	4.93	45.3	90.18	11.42	46.08	80.0	9.46	43.03	81.0	13.26	39.06	74.65
72	4.6	56.45	92.0	4.2	55.4	92.9	3.4	53.4	93.9	3.91	46.32	92.21	6.49	51.02	88.7	4.77	47.84	90.0	5.78	46.54	88.95
96	2.89	58.15	95.0	3.99	55.71	92.31	2.61	54.29	95.41	3.23	47.00	93.56	4.69	52.82	91.8	4.65	48.72	91.0	2.89	49.43	94.47

Table 4. Ignition/rise of temperature on addition of excess water.

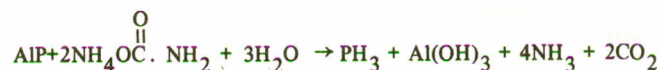
Time in min.	Room Temperature : 23°C Room Humidity : 54 - 56%							
	Phostoxin Degesch (A) °C	Detia Gas Ex-T (B) °C	Fumitoxin (C) °C	Phostoxin R-REPAC (D) °C	*Gastoxin Delecia (E) °C	**Gastoxin Delecia (F) °C	Detia Gas Ex-B (G) °C	
Zero	25	22	22	20	26	24	20	
1	-	-	-	-	-	-	-	
2	-	-	26	35	27	26	-	
3	-	23	29	-	-	-	-	
4	-	-	35	-	-	-	-	
5	25	25	37	45	28	28	30	
6	-	26	41	-	-	-	-	
7	-	-	47	50	29	29	-	
8	-	-	51	-	-	-	-	
9	-	27	55	-	-	-	-	
10	26	28	62	-	30	30	47	(fumes)
12	-	-	65	-	31	31	-do-	
14	-	-	65	-	-	-	-do-	
15	28	-	64	90	32	32	58	
16	-	28	-	96	-	-	58	
17	-	-	-	(dense fumes)	33	33	58	
18	-	29	-	108	-	-	58	
19	-	-	-	-	34	34	58	
20	28	30	60	100	36	37	60	
21	-	-	59	(water condensed)	-	40	-	
22	-	-	-	95	40	(dense fumes)	70	
23	-	-	-	-	50	50	-	
24	-	31	-	70	(ignition)	(ignition)	80	
25	-	32	55	-	-	-	(dense fumes 95°)	
30	-	34	50	65	-	-	80	
35	28	40	(no fire, no explosion)	55	-	-	75	
40	29	47	(no fire, no explosion)	-	(ignition)	(ignition)	70	
45	41	65	(no fire, no explosion)	-	-	-	55	
50	-	62	(no fire, no explosion)	42	-	-	50	
60	42	52	(no fire, no explosion)	(no fire, no explosion)	-	-	(no fire, no explosion)	

65	-	43
75	70	(no fire, no explosion)
80	90	
85	82	
90	58	
100	40	
105	(no fire, no explosion)	

* Made in India ** Made in East Germany

caught fire with explosive violence. Sample D attained a maximum temperature of 108°C but it did not catch fire.

A, B, C and D contain ammonium carbamate whereas E, F and G contain urea and sodium chloride. Ammonium carbamate decomposes [5] under the influence of heat in a short while almost completely and directly from the solid to the gaseous condition. The gaseous substances formed in this case are ammonia and carbon dioxide. The latter particularly lowers the possibility of spontaneous ignition:



of hydrogen phosphide formed in the presence of excess water. They also add to accelerate respiration which is a desirable property for fumigation. Urea and sodium chloride, however, are unable to prevent spontaneous ignition of hydrogen phosphide.

It has been found that samples A, B, C and D lost weight upto 11.37, 10.5, 10.1 and 10.4% respectively in 24 hr and only insignificantly increased (to less than 1%) after 96 hr when placed in open air. Samples, E, F and G on the other hand, gained 10.9, 10.7, and 10.5% weight within 24 hr, 22.7, and 23.3 and 16.1% respectively after

(Continued on column 2)

96 hr under similar conditions. The increase in weight in A, B, C, and D, is possibly the result of the decomposition of ammonium carbamate into gaseous ammonia and carbon dioxide.

It may be concluded from the foregoing discussion that two types of formulation are available in the country: A, B, C and D containing ammonium carbamate and F and G containing urea and sodium chloride. The difference between the two sets is only of degree and not of material. The effect of the presence of carbamate in A, B, C and D is substantial since it is effective in protecting the tablets from spontaneous ignition on adding water. The reaction with water is violent in the case of E and F because after 21–25 min the phosphine evolved catches fire.

Discrepancies have been noted in terms of the claimed and found percentages of active ingredient, whereas A, B and E contain higher quantities, C, D, F and G have lower aluminium phosphide than claimed.

The efficiency of release of hydrogen phosphide in 24 hours is maximum in the case of A, B, C and D whereas in the case of E, F and G it is 76.8, 73.0 and 73.62% respectively.

The maximum release of phosphine is lower in the case of D, E, F and G compared with A, B, and C. On the contrary the release of hydrogen phosphide in the first hour is higher in the case of D, E, F and G and lower in A, B, C. For B the release of hydrogen phosphide is the

lowest amounting to only 0.5% which is quite desirable for workers exposed to phosphine hazard.

The maximum amount of gas released is highest in the case of A; 34% followed by B, 32.66% and C 31.83% and in the case of D, E, F and G it is 27.65, 30.97, 28.05 and 29.08% respectively after 96 hr.

All tablets leave a residue containing aluminium phosphide even after 96 hr but it is higher in the case of E and F compared with A, B, C, D and G.

The above comparative data seem to indicate that ammonium carbamate containing tablets do carry advantage over those having urea and sodium chloride.

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