BIOLOGICAL EVALUATION OF BROMOPHOS FOR THE CONTROL OF STORAGE PESTS

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ABSTRACT: The OP compound, bromophos (O-(4-bromo-2,5-dichlorophenyl)-O,O-dimethyl phosphorothioate), brand name Nexion(R), has been used for a number of years for the control of storage pests. Because bromophos is able to break the resistance to some other chemicals it can be considered a useful alternative in this field of application.

Bromophos may be applied directly to the stored products, to bagged goods or in empty stores. For the various fields of application a number of formulations is available: emulsifiable concentrate and dust for admixture, emulsifiable concentrate and wettable powder for bags and empty silos.

Experiments and experience from practical use in many countries have established the effectiveness of the material against most of the storage pests for protection periods of at least one year using a dosage of 12 ppm admixed to small grain and 8 ppm to corn and beans. For bag treatment 1-1.25 g a.i./m^2 bag surface, and for empty storage bins 0.5 - 1 g a.i./m^2 wall surface are recommended.

Apart from its effectiveness against insects bromophos is distinguished by low mammalian toxicity. Existing residue data afford favourable tolerances. The refined grade bromophos used for this purpose does not cause taint taste problems.

INTRODUCTION: First data encouraging the development of bromophos as an insecticide for the protection of stored grain were presented by Immel and Geisthardt in 1964 [1]. They emphasized the insecticidal potential, the low mammalian toxicity and the persistence on alkaline surfaces. During the following years quite a body of data on the efficacy against the main species of storage pests was accumulated in laboratory work. In addition some of the more specific problems of a storage pesticide were studied, e.g. persistence on various surfaces, influence of temperature and moisture content of the grain on performance and resistance behaviour.

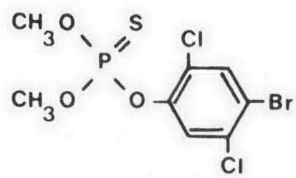
As soon as the results of some of these studies revealed the potential of bromophos as a grain protectant, field evaluations were initiated in order to obtain practical recommendations for the treatment of empty storage rooms and for the protection of stored grain in bag stacks as well as in bulk.

Meanwhile the needed data on toxicology, metabolism. residue behaviour and taint problems were generated. [2,3,4,5]

Bromophos has been developed and is marketed in various formulations under the brand name of Nexion(R) by Celamerck.

CHEMICAL AND TOXICOLOGICAL PROPERTIES OF BROMOPHOS: As the chemical and toxicological properties have been described in full detail [2,4] they are summarized in the following way:

Chemical name:	0,0-dimethyl-0-2,5-dichloro-4-bromo=phenyl-thionophosphate
Structural formula:	



Molecular weight:	365.9
Appearance:	white, crystalline substance
Melting point:	53 - 54°C
Boiling point:	140 - 142°C at 10^{-2} mm Hg
Vapour pressure:	1.3×10^{-4} mm Hg at 20°C
Solubility:	soluble in most organic solvents, hardly soluble in alcohols of low molecular weight, in water 40 ppm at room temperature
Acute toxicity:	LD_{50} oral on rat 3750-7700 mg/kg bodyweight LD_{50} dermal on rabbit 2188 mg/kg bodyweight
Subacute toxicity:	The no-effect level (cholinesterase inhibition in erythrocytes) is 3.0 mg/kg/day for dogs and 2.5 mg/kg/day for rats.
Chronic toxicity:	No clinical symptoms (except cholinesterase inhibition) up to 350 mg/kg/day on rats and up to 87.5 mg/kg/day on dogs.

LABORATORY EVALUATION OF BROMOPHOS: As pointed out by Immel and Geisthardt [1] bromophos is a rather slow-acting material. This fact must be taken into consideration when comparative test results are being evaluated.

In extensive laboratory studies good insecticidal and acaricidal activity has been established for the most important storage pest species, which are listed below:

Coleoptera	*Acanthoscelides obtectus* (Say)
	Cryptolestes ferrugineus (Stephens)
	Gnathocerus sp.
	Lasioderma serricorne (Fabricius)
	Oryzaephilus mercator (Fauvel)
	Oryzaephilus surinamensis (Linnaeus)
	Ptinus tectus Boieldieu
	Rhyzopertha dominica (Fabricius)
	Sitophilus granarius (Linnaeus)
	Sitophilus oryzae (Linnaeus)
	Sitophilus zeamaize Motschulsky
	Stegobium paniceum (Linnaeus)
	Tenebrio molitor Linnaeus
	Tenebrioides mauritanicus (Linnaeus)
	Tribolium castaneum (Herbst)
	Tribolium confusum Jacquelin du Val
	Trogoderma granarium Everts
Lepidoptera	*Cadra cautella* (Walker)
	Ephestia elutella (Hübner)
	Ephestia kuhniella Zeller
	Sitotroga cerealella (Olivier)
Acarina	*Acarus siro* Linnaeus
	Glycyphagus destructor (Schrank)
	Tyrophagus putrescentiae (Schrank)

Results on topical application - Screening 16 compounds for the susceptibility of *T. confusum* and *T. castaneum*, Lemon [6] classified bromophos as belonging to the activity group of the standard material malathion for both species, the LD_{50} values being calculated on the basis of a 6-day count.

Lemon [7] selected then malathion, bromophos and fenitrothion for a detailed testing on 10 species of stored product beetles. Fenitrothion showed superior activity. Bromophos and malathion exhibited similar efficacy on *T. confusum, T. castaneum, S. granarius* and *S. zeamaize*. As compared with malathion, bromophos was slightly more active against *L. serricorne* and *P. tectus* while it was less effective against *R. dominica, S. paniceum, O. surinamensis* and *O. mercator*. The short period of 3 days elapsing between treatment and assessment may partly account for the relatively poor performance on the two *Oryzaephilus* species.

Persistence of bromophos on various types of surfaces -

Activity on filter paper and wooden panels: A number of species were submitted to a test on filter paper, on painted and unpainted wooden panels at room temperature. Bromophos was applied as a 40% ec formulation. The insects were kept for one hour on the deposit. Insect mortality was determined one or two days thereafter. The following species showed high degrees of mortality:

	on filter paper	on wooden panel	source
	dosage in g a.i./m^2		
C. ferrugineus	0.142		[8]
O. surinamensis	0.128	0.198	[9]
S. granarius	0.128	0.198	[9]
S. granarius	0.142		[8]
S. paniceum	0.128	0.198	[9]
T. molitor	0.128	0.198	[9]
T. confusum	0.128	0.198	[9]
E. elutella	0.128	0.198	[9]

Bromophos performed always better than the standard lindane used at the same dosage except in a few cases on painted wooden panels on which lindane was slightly superior.

In other tests on filter paper bromophos wp at deposits of 0.75 and 1.5 g a.i./m^2 maintained very high mortalities on *T. confusum* for periods of up to 16 weeks [7]. Bromophos was as persistent as fenitrothion and slightly superior to malathion at equal dosages.

Residual toxicity of bromophos in acetone solutions applied to paper aluminium foil panels was determined for adults of *L. serricorne* in an 8-hour exposure. On a deposit of about 1 g a.i./m^2 mortality figures of 97% and 100% were obtained on deposits aged for 5 and 28 days, respectively [10].

The influence of temperature on insecticide toxicity was determined on impregnated filter papers [11]. At temperature levels of 26.7, 15.5 and 10.0°C five species of beetles were exposed to the deposits for 24 hours; 72 hours thereafter mortality was assessed. Bromophos and malathion showed positive temperature coefficients for all species under test. Bromophos revealed the minimum of activity at 10.0°C, it increased at the 15.5°C level and reached the maximum at the higher temperature. This toxicity-temperature gradient of the compound is parallelled by the biological activities of the insect. It is noteworthy that at low temperatures the toxicity of bromophos on *T. confusum* and *T. castaneum* decreased more than on *C. ferrugineus* and *O. mercator* while *O. surinamensis* held a medium position between the two extremes.

Persistence of bromophos on concrete: Concrete blocks were treated with 25% wp formulations of bromophos, malathion and fenitrothion at rates of 0.75 and 1.5 g a.i./m^2. Mortality figures of *T. confusum* exposed for 6 days indicated that malathion showed negligible toxicity after 1 week for both dosage rates, while fenitrothion exhibited a 20% mortality after 24 weeks at the higher dosage. At the same time the lower bromophos dose produced a mortality well above 95%. The extremely good persistance of the higher bromophos rate guaranteed an efficacy of 95% over a period of 40 weeks. In view of the results obtained from tropical application bromophos demonstrates an unique degree of persistence on alkaline surfaces [7].

Activity of bromophos in stored products - Screening dust formulations for the control of *A. obtectus* on haricot beans, bromophos revealed appreciable efficacy at a 1 ppm rate and 4 ppm prevented completely the emergence of F_1 beetles [12].

In a trial in Uganda, maize with moisture content of 11% was treated with a 2% dust formulation of bromophos at 6.25 and 12.5 ppm. The biological performance on *S. oryzae* was compared with malathion at the same doses and lindane at 1.25 and 2.5 ppm. Both dosages of bromophos and malathion kept the insect population at a low level during the test period of 32 weeks while lindane failed after 11 weeks. The germination rate of the maize stored for 32 weeks was 90% for both rates of bromophos and 80 and 70% for the lower and higher malathion rate, respectively [13].

In a small scale trial on wheat with a dust formulation of bromophos complete kill was obtained for *T. confusum, Cryptolestes* sp. at a dose of 7.5 ppm and for *T. granarium* and *Gnathocerus* sp. at a rate of between 7.5 ppm and 15 ppm. The activity of bromophos was superior to DDT, lindane and carbaryl and equal to malathion for all mentioned species except for *Cryptolestes* which was more susceptible to lindane and malathion [14].

Using a 2% dust formulation on wheat of 12% moisture content Lemon [7] observed good initial control of *S. granarius* adults at a dosage as low as 4 ppm, the mortality degree increased at 8 ppm. The increase of control of adults corresponded to the decrease of number of larvae which emerged from the wheat.

The efficacy of a 40% ec bromophos formulation was evaluated against *S. granarius* and *O. surinamensis* on 45 kg lots of wheat (moisture content from 14.0% to 12.3%) and barley (13% m.c.). A considerable degree of mortality over a period of 16 weeks was recorded for both species at all tested dosages of 8, 16 and 24 ppm. After 24 weeks of storage the efficacy against *O. surinamensis* was nearly identical with all tested dosages on wheat and barley whereas a better effect could be found against *S. granarius* on barley than on wheat [15].

The same authors describe the results of a large scale field trial and compare them with the findings of the laboratory trials. In a metal bin wheat of 15% moisture content was heavily infested with *O. surinamensis* and was heating up to 42°C. Eight and 16 ppm of 40% ec bromophos was the application rate. After a slow initial action, the mortality after 24 hours averaged 97% at the lower and 93% at the higher rate. In bioassays both treatments gave 100% mortality up to 52 weeks. Of both trials, chemical assays were carried out. The initial degradation rate of bromophos in wheat and barley in the small scale trial was much faster - especially during the first month - than in the trial on bulk wheat. This difference in breakdown behaviour was reflected in the poorer control in the small scale trial [15].

The influence of temperature on the activity of bromophos was evaluated by bioassaying treated wheat. Contrary to the results obtained on filter paper [11] it was found with grain that the effect against *E. kuhniella*, *S. oryzae*, *T. confusum*, *T. granarium* and *R. dominica* was better at lower temperatures (cool storage) than at the higher temperature of 26°C [16].

The influence of moisture content of the grain on persistence of bromophos and malathion was determined in trials applying 10 and 20 ppm to warm (30°C) and moist wheat of 18% moisture content. Bioassaying the samples with *O. surinamensis*, it was found that bromophos lost activity after 6 weeks to the same extent as malathion after 2 weeks [15].

Penetration of bromophos into wheat grains was studied by applying bromophos in hexane solutions either topically to individual grains or by wetting them uniformly. More than half of the intact bromophos had penetrated to the endosperm within one hour and after 36 hours up to 25% had entered the germ, which are considered the main sites of degradation. While over the next 12 days the amounts of bromophos were decreasing in those two sites the deposit in and on the pericarp remained constant. The total quantity of intact bromophos on the grain decreased during those 14 days to approximately half the original level. The site of application influenced the rate of breakdown. Penetration occurs more rapid when applied to the attachment region and in the crease area than when administered to the back or brush areas [3].

Eichler, who was able to confirm largely the results of Rowlands in his chemical studies, found similar penetration behaviour for ec and wp formulations of bromophos [5]. Parallel insecticidal assessments using *T. confusum* and *S. granarius* indicated that there was no difference in activity between the two formulations; at both the 8 and 12 ppm application rate the mortality was better than 95% after 12 months of storage [17].

A bromophos emulsion used at a dosage of 12 ppm on grain showed complete kill of *G. destructor* and considerable potential against *T. putrescentiae* and *A. siro*. The mortalities obtained on *T. putrescentiae* were between 75 and 100%. It is of interest to note that *A. siro* was not affected at all during an exposure time of 7 days while a mortality rate of about 50% was obtained within an exposure period of 14 days [18].

<u>Resistance situation of bromophos</u> - Resistance of many important storage pests to extensively applied insecticides was summarized on a recent FAO meeting [19]. Some data on cross-resistance of alternate insecticides to already established pesticides are also available.

As far as bromophos is concerned, Dyte and Rowlands indicated [20] that bromophos was effective against the malathion-resistant strain of *T. castaneum* found in Nigeria. Later some malathion-resistant strains showed cross-resistance to bromophos [21]. In all instances, these malathion-resistant strains were found to have lindane-resistance also.

In Australia malathion and lindane resistance was found in *T. castaneum* derived from peanuts. Although these strains showed an appreciable degree of tolerance to a large number of insecticides no significant change in tolerance to bromophos could be detected [22]. These findings were confirmed on other strains [19].

Bromophos showed the same toxicity on malathion-resistant and susceptible strains of *T. castaneum*. The LD_{50} figures for both bromophos and its metabolite bromoxone were of similar magnitude [23].

Malathion-resistant strains of *T. confusum* of Australian origin did not show resistance to bromophos (Campbell-Brown and Champ, in 19).

Strains of *S. oryzae* and *S. granarium* from Australia, which showed various degr-es of resistance to malathion, diazinon, lindane and other compounds were not resistant to bromophos (Campbell-Brown and Champ, in 19).

A malathion-resistant strain of *R. dominica* from Australia did not exhibit any resistance to bromophos (Campbell-Brown and Champ, in 19).

Various degrees of tolerance to a number of OP-esters including bromophos have been observed on strains of *Oryzaephilus* sp. from various locations (Tyler and Binns, Campbell-Brown and Champ, Dyte and Forster, in 19).

C. cautella which could not be controlled on South African maize by 10 ppm malathion was completely controlled by dosages of 5 and 10 ppm bromophos [24].

On the basis of available knowledge on the resistance situation of bromophos this material can be considered as a useful alternative to some of the insecticides which are now in use for the control of storage pests.

FIELD EVALUATION OF BROMOPHOS: An extensive field trial programme has been carried out in Argentina, Australia, Canada, France, Germany, Kenya, Malawi, Mexico, Nigeria, South Africa, Spain, Tunisia and Yugoslavia. Some of the results obtained are reported in this paper.

As far as the choice of formulations is concerned it must be stated that in all cases in which stored produce destined for human consumption is likely to get into direct contact with Nexion the use of formulations containing bromophos refined grade is advisable to avoid possible taint and taste risks.

Treatment of empty stores - In Yugoslavia Ilic and Popovic [25] carried out an extensive test programme treating concrete, of painted or lime-washed brick walls and of wooden panels. *S. granarius*, *S. oryzae*, *T. confusum*, *T. castaneum* and *O. surinamensis* were included in the test. All pest species were completely eliminated from the storage rooms by a 1 g a.i./m^2 rate of bromophos 40% ec. The performance of bromophos was superior to that of malathion at 1 g a.i./m^2 and lindane at 3 g a.i./m^2. The efficacy of deposits on concrete walls was emphasized.

Watters [26] has evaluated the effectiveness of bromophos for the control of insect pests in Canadian terminal grain elevators by spraying bromophos wettable powder and malathion at rates of 1.46 g a.i./m^2. He used *T. confusum* adults for bioassay.

concrete floors both materials performed well over a 10 week period. After 33 weeks bromophos on the painted parts of floors exhibited more toxicity than malathion. The relatively poor performance of bromophos on the unpainted floor parts is attributable to the low pH-level of 5.9 - 6.2 in the concrete.

For practical purposes 0.5 - 1.0 g a.i./m^2 of a wettable powder formulation should be sprayed on walls before the grain is placed in the bin.

Protection of bag stacks - In Malawi two trials on small stacks of bagged maize and one trial on large stacks were conducted with bromophos 25% wp for the control of *C. cautella*. In the two small scale trials the stacks were convered by a hessian sheet on which one spray at a rate of 3 g a.i./m^2 was applied. For the storage period of about 2 months bromophos showed much better effect than the standard treatment with lindane/malathion. In the large scale trial bromophos was applied to the bags at a rate of 0.75 g a.i./m^2 at monthly intervals. Again the pest control of the bromophos treated stacks was superior to the malathion/lindane treatment at weekly intervals. It is concluded by Schulten [27] that bromophos must be applied at 2 - 4 week intervals at a dosage which is higher than 0.75 g a.i./m^2.

For further work we propose to apply bromophos at rates of 1.0 to 1.25 g a.i./m^2. Depending on the desired period of protection additional sprays must be applied at intervals which must be determined for each particular set of conditions. A wettable powder formulation of bromophos refined grade is recommended.

Protection of bulk grain - In Spain bromophos ec 36 at 9 ppm effected 100% control of *Cryptolestes* sp., *S. oryzae*, *S. granarius* and *R. dominica* over the storage period of 10 weeks throughout the 2.50 meter high bulk of wheat. In a similar trial 12 ppm of bromophos produced complete control of *O. surinamensis*, *S. granarius*, *S. oryzae* and *T. molitor* in wheat for 5 months [28].

Australian wheat of a moisture content below 10% was treated with 6 and 12 ppm of bromophos and 12 ppm of malathion against *R. dominica*. Up to 6 months the grain was protected by the 6 ppm bromophos dosage while the 12 ppm bromophos rate afforded good control for 14 months. The malathion treatment was not as effective either in initial or in residual efficacy. *S. granarius* was completely controlled by all treatments for the whole 14 months storage period [29].

Bromophos gave good results at 5 and 12 ppm against *S. cerealella* on Australian wheat after 3 months of storage.

Under the subtropical conditions of South Africa, bromophos was tested in direct application to maize in comparison with pyrethrum and malathion. Bromophos 40% ec was applied at 5 and 10 ppm rates. *C. cautella*, *S. oryzae*, *R. dominica*, *T. castaneum* and *O. surinamensis* were the dominant species. Bromophos afforded perfect control of all insect species over a storage period of 50 weeks at both dosage rates with the exception of *R. dominica* which was not completely controlled by the 5 ppm rate. The efficacy was equal to the 1.75 ppm pyrethrum treatment. The bin treated by 10 ppm malathion had to be fumigated due to failure on *C. cautella*. After the 50 weeks storage period the maize showed a 97% germination rate for the bromophos treatment as compared with a 41% figure for the untreated control. There was no difference in flavour in foods prepared from treated and untreated maize [24].

In Nigeria trials were conducted with bromophos on corn on the cob which was stored in cribs on a village farm. A 1% bromophos dust formulation applied at 20 ppm performed equally well as malathion 1% dust at 30 ppm and iodofenphos 5% at 20 ppm for the normal storage period of 6 months. Major pests were *S. zeamaize* and one undetermined moth species. The moth damage was larger during the first four months of storage while the damage by *S. zeamaize* was more pronounced after three months of storage [30].

In a similar test in Malawi using cobmaize treated with bromophos dust 2% at 12 ppm, it was found that the average percentage of damaged grains was 4.8% with bromophos in comparison to 51.8% in the untreated control after a storage period of 4 months. Pirimiphos gave a figure of 3.5% and tetrachlorvinphos of 5.6% [31].

On the basis of all experimental results it is concluded that for storage periods of at least one year the recommended rate for the control of pests in wheat, barley, rice, sorghum, rye etc. is 12 ppm bromophos refined grade and 8 ppm is proposed for the treatment of maize, beans and peas. When a shorter storage period, e.g. half a year, is anticipated a dosage of 6 ppm should be used for all mentioned products. A 1.2% dust and a 36% ec formulation are available for this purpose.

SUMMARY: Bromophos has been developed for the control of pests in stored products.

In laboratory work bromophos revelaed a good broad spectrum insecticidal efficacy against the most important storage pest species - including a number of resistant strains of several insects. It showed good persistence on various types of surfaces as well as on grain.

The results from large scale experiments using bromophos for the protection of empty stores, bag stacks and bulk grain are summarized in dosage recommendations for further work. For spraying of empty stores rates of 0.5 - 1.0 g a.i./m^2 wall surface and for bag treatment dosages of 1.0 - 1.25 g a.i./m^2 bag surface are proposed. Recommended application rates for bulk treatment are 12 ppm on small grains and 8 ppm on maize and beans for protection periods of at least one year. For shorter storage periods 6 ppm should be used on all storage goods.

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