METHACRIFOS - A NEW INSECTICIDE FOR GRAIN PROTECTION

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INTRODUCTION: Methacrifos is an organophosphorus insecticide discovered by CIBA-GEIGY LTD. in Switzerland. The compound acts as as contact, vapour and stomach poison against all important arthropod pests of stored products. It is also highly effective against major malathion- and gamma-HCH-resistant insects. Methacrifos will fill a widening gap in the possibilities of grain protectants in view of the world-wide occurrence of resistance in grain pests to malathion and gamma-HCH.

CHEMICAL FORMULA AND FORMULATIONS: Description of methacrifos (CGA-20168, DAMFIN(R), OMS-2005) BSI and proposed ISO common name: methacrifos

Systematic chemical name: O-2-methoxycarbonylprop-1-enyl O,O-dimethyl phosphorothioate

Structural formula:

Formulations: Formulations used to date have included an emulsifiable concentrate EC 950 (950 g a.i./lt.); a dust P2 (2% a.i.), SCO 1000 (1000 g a.i./lt.) and a ready-to-use formulation SO 050 (50 g a.i./lt.).

TOXICOLOGICAL PROPERTIES: The acute toxicity of technical and formulated methacrifos to laboratory rats is shown in Table I. The technical grade methacrifos and its EC 950 formulation are slightly toxic to rats by oral and dermal administration.

Technical grade methacrifos and its formulations cause no or moderate skin irritations and no or minimal eye irritations in rabbits.

Technical grade methacrifos is practically non-toxic for birds (Japanese Quail). The EC 950 formulation is moderately toxic for birds. The technical grade of methacrifos is highly toxic for rainbow trout, but only moderately to slightly toxic to Crucian carp, Bluegill and guppies. The formulations are distinctly less toxic to fish than the technical material.

conditions showed the thermal conductivity of flue-cured tobacco strips to be ca. 0.60 BTU/hr. ft^2 F/in.

Nearly completed is an experiment designed for the measurement of the specific heat of tobacco. The engineers have designed a test unit where electrical energy is delivered to a plate and it is released to the tobacco as thermal energy, Figure 5. By releasing a measured quantity of electrical energy and by measuring the temperature increase of the tobacco, one may compute the specific heat.

This research investigation is now in the engineering phase and results from these basic studies will be used to establish the design requirements for temperature control systems in tobacco storages to control insects during the winter season. Through modeling, competitive designs will be evaluated and the primary criterions for selection will be the system's operational efficiency and its economical structure.

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Table I
Toxicity of technical and formulated methacrifos to laboratory rats

Preparation	Rat acute oral LD 50 (mg/kg)	Rat acute dermal LD 50 (mg/kg)	Rat acute inhalation LC 50-4h (mg/m^3)
Methacrifos tech.	678	>3'100	>2'200
EC 950	924	>3'100	approx. 2'500
P 2	>10'000	>3'100	>1'800
SO 050	>10'000	>4'600	>3'000

The results from the subacute feeding studies with rats, dogs and poultry are favourable. Long term feeding studies with rats and mice are in progress.

INSECTICIDAL PROPERTIES: Methacrifos shows extremely high insecticidal activity.

Table II demonstrates the spectrum of activity of methacrifos, especially against stored product insects and also its relevant efficacy against malathion and HCH resistant pests. The importance and the occurrence of resistant strains of pests are documented by Champ and Dyte (3).

Direct spraying in a standard Potter spray tower (4) and other experiments have demonstrated the contact activity of methacrifos against beetles, moths, flies, roaches, and mites present in stores (Table III).

A special property of methacrifos is its penetration into grain, by which the internal larval stages are killed (2).

The spectrum of activity of the compound and its various modes of action led to application of methacrifos as residual protectant for admixture with bulk stored products and for desinsectisation purposes in empty stores and warehouses.

FIELD APPLICATIONS: Application of methacrifos as a surface spray: The following experiment was carried out to measure the efficacy of methacrifos as a surface spray.

In storerooms with a capacity of $70m^3$ granary weevils and flour beetles were released in large numbers. The stores were treated one day later with the insecticides (3 formulations of

Table II
LC50 for grain pests after 24h exposure, FAO Method No. 15
(Impregnated filterpaper)

Species (adults)	Strain origin Champ and Dyte (1976)	% a.i. in 0.5ml solvent per 7cm diameter filter paper				
		Methacrifos	Malathion	Gamma-HCH	Pirimiphos-Methyl	Chlorpyriphos-Methyl
Tribolium castaneum:	Australia	0.01	0.78	1.0	0.05	0.03
	Cairo	0.009	0.15	0.27	0.05	0.02
Oryzaephilus surinamensis:	649 N.America	0.05	0.43	0.72	0.58	0.21
	479 W.Asia	0.01	0.21	0.20	0.12	0.03
Sitophilus granarius:	248 S.America	0.003	0.04	0.01	0.04	0.03
	849 W.Asia	0.003	0.06	0.29	0.02	0.03
Sitophilus oryzae:	475 W.Asia	0.006	0.03	0.13	0.13	0.01
	Cairo	0.007	0.01	0.12	0.03	0.12
Rhizopertha dominica:	111 N.America	0.29	10.0	0.02	0.75	0.35
	RD 118 Australia	0.23	5.50	0.05	0.80	0.62
	Basle	0.11	0.44	0.005	0.76	0.36
Acanthoscelides obtectus:	Basle	0.013	0.34	0.21	0.16	0.05
Araecerus fasciculatus:	Nigeria	0.013	0.39	0.19	0.16	0.40

Table III
Spectrum of effectiveness of methacrifos

P E S T	
Coleoptera / beetles	Lepidoptera / moths
Sitophilus granarius, L.	Sitotroga cerealella, Oliv.
Sitophilus oryzae, L.	Ephestia elutella, Hübn.
Sitophilus zeamais, Motsch.	Ephestia kühniella, Zell.
Rhyzopertha dominica, F.	Cadra cautella, Walk.
Tribolium confusum, Duv.	Plodia interpunctella, Hübn.
Tribolium castaneum, Herbst.	Tineola biselliella Hum.
Tenebrio molitor, L.	Orthoptera / cockroaches
Oryzaephilus spp.	Acheta domesticus, L.
Cryptolestes spp.	Blattella germanica, L.
Trogoderma granarium, Everts	Blatta orientalis, L.
Dermestes spp.	Periplaneta americana, L.
Lasioderma serricorne, F.	Acarina / mites
Stegobium paniceum, L.	Acarus siro, L.
Necrobia rufipes, Deg.	Tyrophagus casei, L.
Anthrenus vorax, Waterh.	Tyrophagus putrescentiae, Schr.
Anobium punctatum, Deg.	Glycyphagus destructor, Schr.
Ptinus fur, L.	Glycyphagus domesticus, Deg.
Acathoscelides obtectus, Say	Dermatophagoides pternoyssinus, Tron.
Araecerus fasciculatus, Deg.	
Diptera / flies	
Drosophila spp.	
Piophila casei, L.	

methacrifos, EC 950, SO 050 and P 2) (see Table IV). A mixture of wheat and rolled oats was exposed unpacked on the floor of each room to assess the insecticidal properties of the applied formulation. 1,4,7 and 11 days later, samples of exposed food were taken for checks on infestation rate.

The experiment was successful at dosages of 200-400 mg a.i./m^2. The treatments practically prevented infestation of exposed foodstuffs. This experiment confirmed practical observations.

Application of methacrifos as a space spray: The application of space sprays is a normal method for insect control in various objects such as railway-boxcars, boats, containers and many kinds of empty storerooms. Using this method the spray can be applied

Table IV
Survival and F_1-generation of *Sitophilus granarius* and *Tribolium castaneum* after a clean-out treatment by surface spraying of methacrifos conditions: 22 ± 2° C, 35 ± 5% r.h., 2 replicates

Formulation	Dosage mg a.i./m^2	Number of insects released in store	Total (%) F_1-Generation after 12 weeks in exposed samples				Cumulative F_1-Generation after 12 weeks (%)		Reduction in %	
			1 day	4 days	7 days	11 days	S.gran.	T.cast.	S.gran.	T.cast.
EC 950	200	1000	0	0	0	0	0	0	100	100
	400	1000	1	0	0	0	0	1	100	99
SO 050	200	1000	0	0	0	0	0	0	100	100
	400	1000	0	0	0	0	0	0	100	100
P 2	200	1000	0	0	0	0	0	0	100	100
	400	1000	4	0	0	0	3	1	97	99
Untreated	-	1000	142	49	107	102	100	100	0	0

from outside of the rooms. Methacrifos was applied many times as an indoor space spray. An experiment in which encaged pests of stored grains were exposed in the treated rooms is described here.

The cages, containing *Sitophilus granarius*, *Tribolium castaneum* and *Rhizopertha dominica*, were placed at various positions in empty railway-boxcars. Two formulations of methacrifos namely EC 950 and a ready-to-use spray SO 050 were applied with an RL-Atomist (mistblower) in dosages of 75 and 150 mg per m^3. The EC 950 was diluted with water. The capacity of a railway-boxcar is [illegible] m^3. After a 4 hour exposure in the treated boxcar the encaged insects were transferred to clean jars. The mortality was determined 20 hours later. The actual dosage of a.i. in the cages was checked colorimetrically (UVITEX-method). Air samples were taken 24 hours after application to demonstrate the volatility of methacrifos. Residues of the chemical in the air were present at both formulations and dosages.

The experiment carried out at the harbour of Basle brought successful results concerning the insecticidal activity at dosages of 75-150 mg a.i. per m^3 (see Table V).

Application of methacrifos as a prophylactic grain protectant: Field trials were carried out in several countries in Europe. Wheat, barley and oats were treated with 10 ppm of methacrifos. For the application either an EC 950 diluted in water or SO 050 ready-to-use formulation was sprayed on the conveyor belt with a Vobamatic sprayer or another spray-apparatus. Subsequently the cereals were stored in silos, bins or heaps.

The bioassays, with major grain pests of samples taken in a depth of 2 m, show excellent protection of the grain by methacrifos for several months.

Large scale treatments of stored grain were carried out under commercial conditions in Australia. Thanks to help from C.S.I.R.O., Australia Wheat Board and Queensland Department of Primary Industry, it was possible to treat and store under different conditions thousands of tonnes of various grains.

Table VI summarizes the results of a trial at the experimental station at Kemp's Creek, Australia, where lots of maize, barley, paddy rice and sunflower were treated with 10 ppm methacrifos and stored in 10'000 lt. mini-silos. This trial shows the pattern of degradation of methacrifos in different grains and also the period of protection given by the methacrifos treatment.

Application of methacrifos as a curative grain treatment: The appropriateness of methacrifos for curative treatment of infested grain was shown in several field experiments in Switzerland. The infested goods were imported oats, barley and coffee. Methacrifos was applied as an emulsion or as a powder.

Table V
A comparison of two methacrifos formulations when used for space treatments in empty railway-boxcars; Conditions: 25 ± 1° C, 50-60% r.h.

Cage position	Formulation	Dosage		Test insects					
				S.granarius		T.castaneum		R.dominica	
		Application rate mg a.i./m^3	mg a.i./m^2 measured in cage	Mortality % after 4h	Mortality % after 24h	Mortality % after 4h	Mortality % after 24h	Mortality % after 4h	Mortality % after 24h
Sides	SO 050	75	0.03	100	100	30	70	90	100
		150	0.04	100	100	95	100	100	100
	EC 950	75	0.06	100	100	55	75	85	95
		150	0.06	100	100	90	100	100	100
Floor	SO 050	75	0.14	100	100	25	40	90	90
		150	0.34	100	100	80	95	100	100
	EC 950	75	0.05	90	100	35	80	80	100
		150	0.12	100	100	95	100	100	100
Check	-	-	-	0	10	0	0	0	5

Table VI
Percentage control of F_1-progeny of 4 major pests in a bioassays of various grains stored in mini-silos in Australia with 10 ppm methacrifos; Conditions: 24.5-26.0°C

GRAIN	Test insects Strain origin Champ and Dyte (1976)	Samples taken weeks after treatment 0	6	12
WHEAT	Sitophilus oryzae CSO-231	100	100	100
	Rhizopertha dominica CRD-37	100	99.7	99.6
	Tribolium castaneum CTC-12	100	99.9	99.7
BARLEY	Sitophilus oryzae CSO-231	100	100	99.9
	Rhizopertha dominica RD-118	86.1	97.6	97.4
MAIZE	Sitophilus zeamais wild susceptible strain	100	100	100
PADDY RICE	Sitophilus oryzae CSO-231	99.4	98.9	98.7
SUNFLOWER	Tribolium castaneum CTC-12	100	100	100

Six lots of 50 tonnes of barley and two lots of 50 tonnes of oats were treated with 10 ppm a.i. of EC 950. The figures in Table VII demonstrate the efficacy of the product against *Sitophilus granarius* and *Tribolium castaneum* (see Table VII).

In Table VIII the results are given of an experiment in which barley heavily infested with *Sitophilus granarius* and *Oryzaephilus surinamensis* was treated with 15 ppm a.i. as a P 2 formulation. After the treatment the barley was stored in jute sacks at a temperature of 25° C and a relative humidity of 60-65%. The figures show the excellent activity of methacrifos P 2 formulation

Table VII
Curative efficacy of methacrifos against grain pests in infested barley and oats; Storage conditions: wooden bin, 20-25° C, 6 replicates in barley, 2 replicates in oats.

GRAIN	Formulation Dosage (a.i.)	Infestation rate in treated and untreated cereals live insects/lt. cereal after treatment					
		1 week		3 weeks		9 weeks	
		S.gran.	T.cast.	S.gran.	T.cast.	S.gran.	T.cast.
BARLEY	EC 950 (10 ppm)	1	0	0	0	0	0
	Untreated	15	17	21	15	238	25
OATS	EC 950 (10 ppm)	2	0	0	0	0	0
	Untreated	10	9	11	5	72	20

against granary weevils and saw-toothed grain beetles when applied as a curative measure.

In a semi-practical experiment methacrifos EC 950 was applied in a dosage of 20 ppm of a.i. to coffee beans which were infested by coffee bean beetles *Araecerus fasciculatus*. After the treatment a stock of 25 kg coffee beans were packed in metal drums and stored in 28° C for 4 months. To determine the efficacy of methacrifos against the coffee bean beetle, traps were installed on the top of the drums. The adults emerging over three days were counted in samples taken at various intervals. Table IX gives the figures which confirm the excellent and superior efficacy of the chemical against the coffee bean beetle when curatively applied with 20 ppm.

Table VIII
Curative efficacy of various insecticides in barley against *Sitophilus granarius* and against *Oryzaephilus surinamensis*; Storage: jute sacks at 24 ± 2° C and 60 ± 5% r.h. 3 replicates (Figures: *Sitophilus granarius/Oryzaephilus surinamensis*).

Insecticide Formulation	Dosage (ppm)	Infestation rate in treated and untreated barley Live-insects/1 kg at weeks after treatment					
		3 weeks		10 weeks		20 weeks	
		adults	reduction[a]	adults	reduction[a]	adults	reduction[a]
Methacrifos P 2	15	0/0	100/100	0/0	100/100	0/0	100/100
Malathion P 2	15	0/0	100/100	1/0	92/100	4/55	93/41
Standard 1 P 2	15	0/0	100/100	0/0	100/100	5/0	92/100
Standard 2 P 2	15	0/0	100/100	3/15	77/100	2/136	97/0
Untreated -	-	10/254	- / -	13/245	- / -	59/93	- / -

a) Reduction in % = $100 - \frac{t}{c} \cdot 100$ (t = number of live beetles/sample)
(c = number of live beetles/check)

Table IX
Light-trap counts from infested coffee at various intervals after treatment (Figures = Number of adults of *A. fasciculatus*)

Time after treatment	Product/Formulation/Dosage	
	Methacrifos EC 950 20 ppm	Untreated
1 day	1	16
3 weeks	0	6
6 weeks	0	7
9 weeks	0	10
12 weeks	0	11
15 weeks	-	-
18 weeks	0	19

CONCLUSION: Methacrifos is effective against a broad spectrum of insect pests of stores, and their resistant strains. It can be applied as a surface spray, space spray, prophylactic grain protectant or even as a curative grain treatment. This is an interesting product which fills a real need with its exceptional characteristics. A great demand for it can be expected in the coming decade.

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