

## Some Laboratory Investigations on Bayer 73 and ICI 24223 as Molluscicides\*

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*The authors report on laboratory tests of the chemical properties and molluscicidal activity of the compounds Bayer 73 (70% wettable powder) and ICI 24223 (acid salt and emulsion), and describe the method used for the determination of ICI 24223.*

*It is suggested that field applications of the ICI 24223 acid salt and of Bayer 73 should produce similar results in running and stagnant soft water. Bayer 73 showed a diminution of molluscicidal activity in hard water.*

Various workers (Gönnert & Schraufstätter, 1959; Foster et al., 1960; Gönnert, 1961; Paulini et al., 1961; Schiff, 1961; Webbe, 1961) have reported results of laboratory investigations on the molluscicide Bayer 73 (70% wettable powder). As far as is known few comparable findings have appeared with regard to ICI 24223, apart from the papers by Gillet & Bruaux (1961) and Bruaux & Gillet (1961). The following investigations were done with the object of comparing the molluscicidal and chemical properties of the two compounds in the laboratory.

### PHYSICOCHEMICAL DATA

#### *Determination of the compounds in water*

**Bayer 73 (70% wettable powder).** Strufe's method of determination was used, i.e., saturation with ammonium sulfate, extraction with isobutanol-ethanolamine mixture and determination in a spectrophotometer.

**ICI 24223.** No method for the determination was available but the following was developed in this laboratory:

Measure 50 ml of water containing ICI 24223<sup>1</sup> into a 100-ml separating funnel; add 1 ml of a saturated solution of sodium bicarbonate and 10 ml of purified benzene.<sup>2</sup> Thoroughly shake for about a

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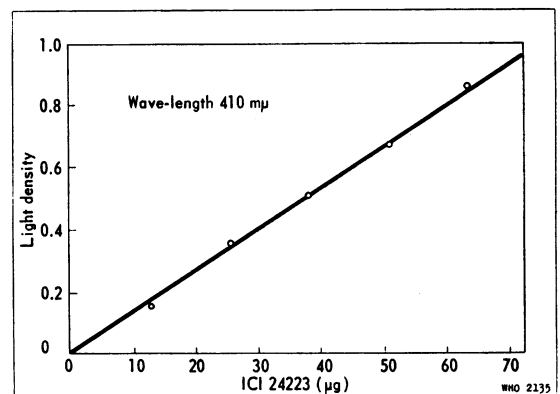
<sup>1</sup> If the water contained more than 1.5 p.p.m. ICI 24223, it was diluted to below this level.

<sup>2</sup> Distil commercial benzene (aliphatic hydrocarbon) on a water-bath; dry the distillate by filtering through filter-paper and shake several times with a few millilitres of concentrated sulfuric acid until the acid remains colourless. Wash the purified benzene with distilled water and filter through filter-paper.

minute. Repeat the extraction with about 5 ml of benzene: filter the extract through a small cotton plug in the stem of a funnel (to absorb any water present) into a dry separating funnel. Add 1 ml of concentrated sulfuric acid to the extract and shake vigorously for 5 minutes. After settling, add 5 ml of a 50% solution by volume of sulfuric acid and mix gently with the concentrated acid at the bottom of the separating funnel. A clear, picric-acid yellow is evident in the acid if ICI 24223 is present. This is measured colorimetrically in a spectrophotometer at a wave-length of 410 m $\mu$  with a light path of 1 cm.

Calibration curves (see the accompanying graph) were drawn up from standards made with the purified base of ICI 24223 in benzene to which distilled water was added and the routine method for the determination followed. Blanks were run at the same time.

RELATION BETWEEN CONCENTRATION OF ICI 24223 BASE AND DENSITY OF LIGHT TRANSMITTED



The yellow colour of the reaction products of ICI 24223 and sulfuric acid was found to be stable.

#### Solubility

**Bayer 73.** The solubility of Bayer 73 (70% wettable powder) at room temperature in distilled water was found to be 1010 p.p.m., which is comparable with the solubility found by Gönner & Straufstätter (1959).

**ICI 24223.** The solubility of ICI 24223 acid salt at room temperature in distilled water was found to be 1320 p.p.m.

The solubility of ICI 24223 base, under the same conditions, was found to be 4 p.p.m.

Solutions of the ICI 24223 hydrochloride were originally clear. With standing, the hydrochloride hydrolysed and the base slowly precipitated until, after four days, the concentration of the solution had dropped from the original 1320 p.p.m. to 170 p.p.m.

#### Dispersion

**ICI 24223 base (40% solution in toluene).** This compound was difficult to disperse in water and a stable emulsion was made by mixing 10 parts each by weight of ICI 24223 (40% in toluene) and naphthenic acid (acid value 170), or oleic and similar acids. To this mixture were added 52 parts by weight of water and 8 parts of concentrated ammonia while stirring. (The emulsion can easily be diluted with water for application.)

#### Adsorption

Approximately 1 p.p.m. of Bayer 73, ICI 24223 (acid salt) and ICI 24223 emulsion (40% in toluene) were used. 500-ml samples of each were shaken with 0.5 g of kaolin for 1 minute and left standing until clear. Controls without kaolin were run simultaneously. The results (Table 1) showed that Bayer 73 was not adsorbed, and ICI 24223 was adsorbed rapidly. Repetition produced similar results.

TABLE 1  
ADSORPTION OF BAYER 73 AND ICI 24223 ON KAOLIN

Molluscicide	Control without kaolin (p.p.m.)	With kaolin (p.p.m.)
ICI 24223 emulsion	1.17	0.448
ICI 24223 acid salt	0.66	0.16
Bayer 73	0.99	0.99

#### Effect of sunlight

Concentrations of 1 p.p.m. Bayer 73 and ICI 24223 acid salt, in clear river water, were divided into: (1) samples exposed to direct sunlight (when not exposed these were kept in the dark at 4°C); (2) samples exposed to the diffuse light of the laboratory; and (3) samples kept in the dark at 4°C. Samples were kept in open Pyrex crystallizing dishes and analysis was done at the same time after all the exposures were completed. It was assumed that breakdown products formed as a result of the action of sunlight did not interfere with the final analysis.

The results (Table 2) showed no significant difference between the breakdown of Bayer 73 and that of the ICI product in hard or soft water. Both compounds were, however, broken down more completely and more rapidly in hard water. This was analogous to the breakdown of sodium pentachlorophenate in hard and soft waters (Meyling et al., 1959) but was not as rapid nor as complete.

In diffuse light and in the dark neither compound had diminished in concentration after 312 hours.

#### Effect of temperature

Samples of approximately 1 p.p.m. of both compounds were kept at 45°C and at room temperature in diffuse light for 13 hours. At the end of this time the concentrations of Bayer 73 were 1.03 and 1.04

TABLE 2  
EFFECT OF SUNLIGHT ON BAYER 73 AND ICI 24223 ACID SALT IN HARD AND SOFT WATER

	Hours exposed to sunlight	Concentration (p.p.m.)			
		Bayer 73		ICI 24223	
		Exp. 1	Exp. 2	Exp. 1	Exp. 2
Soft water	0	1.0	1.01	1.0	0.98
	8	0.90		0.81	
	16	0.80		0.74	
	24		0.67		0.56
	36		0.56		0.40
Hard water	0	1.0	1.0	1.00	1.02
	8	0.71		0.79	
	12		0.58		0.58
	16	0.57		0.59	

p.p.m. respectively, and those of ICI 24223, 1.17 and 1.27 p.p.m. respectively.

#### BIOLOGICAL DATA

##### *Exposure of snails and egg masses*

Similar sized snails (*Biomphalaria* sp.) were exposed in 500 ml of water in crystallizing dishes containing 10-20 snails each. Controls were run simultaneously. A 24-hour period of acclimatization was given the snails in the dishes before molluscicides were added. Fresh solutions of molluscicide were made up for each exposure. After exposure, snails were thoroughly washed and placed in fresh water, and mortality was observed after 24 hours.

*Biomphalaria* egg masses, adherent to thin plastic strips, were exposed to the molluscicides in Syracuse dishes. After exposure the egg masses were washed and placed in fresh water. Eggs were considered non-viable when there was no embryonic movement or when turbid.

##### *Results*

The ICI emulsion was found to be irritant to snails and they left the water (this was probably due to the naphthenic acid or the ammonia in the emulsion). Results are therefore based on the acid salt of ICI 24223 only.

During the summer, using wild snails, 1 p.p.m. each of Bayer 73 and ICI 24223 gave 100% snail mortality in 1½ and 3 hours respectively; at concentrations down to 0.1 p.p.m., Bayer 73 gave a 100% mortality in 5-8 hours while ICI 24223 did not give a 100% mortality between 8 and 20 hours.

Concentrations of 1 p.p.m. and 10 p.p.m. of ICI 24223 had no effect on snail egg masses. They developed normally to hatching both in fresh solutions changed daily and in unchanged original solutions, but the young snails died on hatching. The compound therefore retained its molluscicidal property.

Egg masses exposed to 1 p.p.m. of ICI 24223 for 8 hours and then transferred to fresh water developed normally and the young snails died soon after hatching, suggesting that the compound was absorbed or adsorbed by the material surrounding the egg-capsules. Control egg clutches were used at the same time in the same water as the ICI compound was made up in. The baby snails lived until discarded a week after hatching.

Bayer 73 was found to be 100% ovicidal at 1 p.p.m. in 4-5 hours. At 3 hours the ovicidal effect was not found to be 100%.

##### *Effect of hard and soft water*

Natural waters and tap water were used during winter. Table 3 shows that Bayer 73 at 0.5 p.p.m. had almost no molluscicidal effect in the hard water used. Similar results were obtained with repetition and with 1 p.p.m. concentrations.

TABLE 3  
MOLLUSCICIDAL EFFECT OF BAYER 73 AND ICI 24223  
IN HARD AND SOFT WATER

Water	Conductivity (micro-mhos)	Alkalinity (as CaCO <sub>3</sub> )	Total hardness (as CaCO <sub>3</sub> )	pH	No. snails killed out of 20 after 3 hours in 0.5 p.p.m. of:	
					Bayer 73	ICI 24223
Hard	950	488	408	8.4	4	17
Soft	64	33	26	7.7	17	16
Tap	144	66	71	8.2	16	16

#### CONCLUSIONS

From findings in this laboratory, field applications of the ICI 24223 acid salt and of Bayer 73 wettable powder should produce similar results in both running and stagnant soft water. The ICI 24223 emulsion might produce somewhat different results in running water because of the irritant effect which caused snails to leave the water. The base of ICI 24223 would probably be ineffective as a molluscicide in running water unless applied in solution. The property that ICI 24223 was found to have, whereby the base slowly precipitated from the acid salt, might be turned to advantage by formulation or application methods to produce a molluscicide having a long residual effect in standing water.

The poor molluscicidal activity of Bayer 73 in hard water is a serious disadvantage and has unfortunately been found to be possibly true in the field where, three days after a 24-hour continuous application of 1 p.p.m. of Bayer 73, living adult *Biomphalaria* and *Lymnaea* sp. were found in a little creek (total hardness 950 p.p.m.) a few feet below the application site. Chances of their having come down from upstream were ruled out but they may have been protected by seepage coming into the creek where they were found.

## RÉSUMÉ

L'article apporte les résultats d'une étude comparative, chimique et biologique, de deux molluscicides — Bayer 73, poudre humectable à 70%, et ICI 24223, sel acide et émulsion. Il est à noter que les résultats mentionnés ne portent que sur le sel acide de ce dernier produit, car en émulsion il provoque la fuite des mollusques par suite d'un phénomène d'irritation dû probablement à la présence d'acide naphthénique. L'étude physico-chimique a porté successivement sur le dosage par spectrophotométrie (les auteurs décrivent la méthode originale qu'ils ont imaginée pour ICI 24223), la solubilité, la dispersion, l'absorption, les effets de l'exposition à la lumière et de la température. Les résultats sont très voisins pour les deux produits dont la désagrégation est par ailleurs comparable, bien que plus rapide et plus complète dans les eaux dures.

La mortalité à 24 h a été recherchée sur *Biomphalaria* sp., mollusques et œufs. Appliqués en été sur des mollusques sauvages à la concentration de 1 p.p.m., Bayer 73 et ICI 24223 ont donné un résultat de 100% en respectivement 1½ et 3 h. A 0,1 p.p.m., Bayer 73 exerçait les mêmes effets molluscicides en 5-8 h, tandis qu'au bout

de 8 à 20 h le pourcentage 100% n'était pas atteint avec ICI 24223.

Agissant sur les œufs des vecteurs à des concentrations qui ont varié de 1 à 10 p.p.m., ICI 24223 n'empêchait pas leur évolution, mais les produits étaient détruits au fur et à mesure de leur éclosion, sans doute par contact avec le produit fixé aux enveloppes ovariennes. En comparaison, Bayer 73 à la concentration de 1 p.p.m. détruit la totalité des œufs en 4-5 h, résultat qui n'est pas encore complet à la 3<sup>e</sup> heure.

Ainsi, en application pratique dans les eaux douces, courantes ou stagnantes, l'un et l'autre produits ont des propriétés équivalentes. En revanche, appliqué à la concentration de 0.5 p.p.m., le Bayer 73 n'a pas le moindre effet molluscicide dans les eaux dures; il en est de même à 1 p.p.m., comme l'ont montré des essais répétés. C'est là un sérieux désavantage qui a été vérifié sur le terrain lorsque des adultes de *Biomphalaria* et *Lymnea* sp. ont été retrouvés vivants à quelques mètres du point d'immersion du produit, trois jours après administration maintenue 24 h à la concentration de 1 p.p.m.

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