

# Overview of undesirable effects of using diatomaceous earths for direct mixing with grains

Zlatko Korunić

*Diatom Research and Consulting Inc., 14 Tidefall Dr. Toronto, ON M1W 1J2, Canada*  
Corresponding author: zkorunic@rogers.com

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## SUMMARY

Despite numerous advantages of diatomaceous earth (DE), its use for direct mixing with grains to control stored-product insects remains limited because of some very serious obstacles and disadvantages. The main obstacles preventing a wider use of DEs for mixing with grain, such as health concerns, the reduction in bulk density, differences in insect species tolerance to the same DE formulation, the effects of grain moisture and temperature on the effectiveness against insects, the influence of various commodities on DE efficacy, the use of DEs in some other fields, and possible solutions for overcoming DE limitations during direct mixing with grains are described in this manuscript. The same attempts have been made to discover new ways of increasing significantly the effectiveness against insects when much lower concentrations are used for direct mixing with grains. If these newer enhanced formulations can respond to the existing limitations of diatomaceous earth, a wider utilization of diatomaceous earth may be expected to control stored-product insect pests.

**Keywords:** Diatomaceous earth; Stored products; Grain; Pest control

## 1.1 INTRODUCTION

Diatoms are a major group of algae, the most common types of Phytoplankton. There are more than 200 genera of living diatoms. It is estimated that there are approximately 100,000 of extant species and they are all different in shape and size (Round et al. 1990). Most diatom species are unicellular. Cell wall is made of silica (hydrated silicon dioxide/amorphous silicon). Mostly they live up to a few weeks in salt and fresh water, die and sink to the bottom making pure layers made of diatom bodies. Lakes and sea water have gradually disappeared and the layers of dead diatom bodies are covered with soil and vegetation. The organic tissue of diatoms degrades

with time and the final results are diatom skeletons (fossils) made of amorphous silicon dioxide. These layers of fossilized diatoms are called diatomaceous earth (DE). DE may be different in color because of different minerals and impurities. Sometimes layers are very thick, up to a few hundred meters. Nowadays layers are approximately 20 to 80 million years old (Round et al. 2000). First publications about the use of DE in stored grain protection were published early in the 20<sup>th</sup> century (Calvert, 1930; Zacher & Kunike, 1931; Chiu, 1939a,b; Flanders, 1941; Alexander et al. 1944a,b,c; Korunic, 1998, 2013). From that time, hundreds and hundreds of research papers have been published in many international journals.

During the last 20 years DE has been the subject of several review papers, as well (Quarles, 1992; Golob, 1997; Korunic, 1998; Subramanyam & Roesli, 2000; Fields & Korunic, 2000; Quarles & Winn, 1996; Nikpay, 2006; Korunic, 2013; Shah & Khan, 2014) with numerous references cited in each review. Such comprehensive lists of hundreds of references show a great interest in research of DE as a safe grain protectant. Mostly, the advantages of DE use were described as: natural inert material, safe and effective insecticide, its physical mode of action and long persistence not leaving hazardous residues, and very often with conclusions that DE is a promising insecticide.

The most extensive research of DE has been conducted by numerous researchers in the field of protection of stored agricultural products (Korunic, 1998, 2013; Kljajic et al., 2010; Andrić et al., 2012). The use of DE for structural treatment in stored product facilities was studied by Desmarchelier et al. (1992), Wright (1990), McLaughlin (1994), and Bridgeman (1994).

However, DE is not commercially widely used for direct mixing with grains because of several great obstacles and disadvantages described in this manuscript.

## 1.2 MAIN OBSTACLES TO USING DIATOMACEOUS EARTHS FOR DIRECT MIXING WITH GRAINS

### 1.2.1 Health concerns

A good overview of occupational health and safety issues concerning silica is presented in the publications of NOHSC (1995), and IARC (1997).

Depending on its source and processing, DE may contain from 50 to 0.1% crystalline silica, although DEs registered as insecticides generally have less than 6% crystalline silica, or in some countries less than 1%. Crystalline silica has been shown to be carcinogenic if inhaled (IARC, 1997); therefore, the main hazard to workers is from inhaling dust particles. The issues of importance are: the amount of dust, its particle sizes and extent to which any given DE product contains crystalline silica. The use of proper dust masks to protect workers against inhalation, or the use of low crystalline silica DE can protect against this health risk (Desmarchelier & Allen, 2000). However, particles smaller than 5 microns belong to respirable dust which usually contains the highest quantity of crystalline silica. After application and loading or

unloading in storages, they float in the air for hours. These particles make a real hazard when inhaled directly into the lungs by operators, which causes lung inflammation or even silicosis (NOHSC, 1995; IARC, 1997).

### 1.2.2 Reduction in bulk density

One of the greatest disadvantages and obstacles to using DE as a grain protectant is its unacceptable effect on grain flowability and especially its reducing grain bulk density (test weight). An addition of DE to grains creates a greater friction between kernels, which affects their test weight and flow properties. According to the Canadian Grain Commission, test weight is an extensively used grading factor (Canadian Grain Commission, 2015). The DEs property of reducing test weight makes the grain industry reluctant to use DE for direct mixing with grains. Even very low doses of DE without any insecticide activities still have a significant reducing effect on wheat test weight (Table 1).

Bodroža-Solarov et al. (2011) investigated the quality parameters of several wheat grain lots (low vitreous and high vitreous grains, non-infested and infested with rice weevils (*Sitophilus oryzae* L.) treated with inert dusts (DEs and natural zeolite). They found that the inert dust treatments produced different effects regarding test weight. A principal component analysis (PCA) of data sets was able to distinguish among the various treatments of wheat lots. It was revealed that inert dust treatments produced different effects depending on the degree of endosperm vitreousness.

In a later study, Bodroža-Solarov et al. (2012) confirmed that the most disadvantageous effect of wheat treatments with zeolite and DEs is the test weight reduction. The percentage of test weight reduction is greater in mealy wheat grain than in high vitreous wheat grain. The content of SiO<sub>2</sub> in the inert dust-treated wheat samples was significantly higher in the wheat lots damaged by insects as a consequence of larger accumulation of inert dust in kernel interior through holes produced by insects. However, they also found out some positive effects of wheat treatment with inert dusts through significant improvements of rheological parameters: moisture absorption in the non-infested wheat and flour (dough), and particularly through a rise in dough energy.

Korunic et al. (1998) determined that even very small concentrations of DE from 10 to 50 ppm significantly reduced bulk density (Table 1).

**Table 1.** The reducing effect of very small concentrations of DEs on wheat test weight (Korunic et al., 1998)

Dose (ppm)	DE formulation			
	Celite 209		DiaFil 610	
	Bulk density kg/m <sup>3</sup> ± S.E.M.	Reduction (%)	Bulk density kg/m <sup>3</sup> ± S.E.M	Reduction (%)
0	784 ± 0.6	-	784 ± 0.6	-
10	772 ± 2.6	1.8	774 ± 0.4	1.3
25	763 ± 0.4	2.7	766 ± 0.5	2.3
50	749 ± 1.2	4.5	766 ± 2.3	2.3

DEs applied at 100 and 500 ppm significantly reduce test weight of different commodities (Table 2). The higher concentration of 500 ppm reduced the bulk density of wheat grains for more than 6 kg per hl and barley for 4.7 kg/hl (Table 2). The reducing effect on test weight of oat, and especially maize, was significantly smaller (Korunic, 2007b). Therefore, DEs probably may be used for direct mixing with maize to control insects with lower negative impact in terms of test weight reduction. However, to control insects on maize, higher concentrations of DEs are needed in comparison with the concentration used on wheat (Korunic, 2007b).

**Table 2.** The reduction in bulk density of various grains treated with an effective diatomaceous earth as compared to untreated grain (Korunic, 2007b)

Commodity	Grain density (kg/hl±SEM)		
	0 ppm	100 ppm Reduction in kg/hl	500 ppm Reduction in kg/hl
Oats	62.7±0.4	1.0	3.2
Barley	64.7±0.3	2.3	4.7
Rye	75.4±0.5	2.3	4.3
Maize	64.3±0.2	1.4	2.0
Durum	78.5±0.5	4.2	5.8
Wheat CWRS	81.0±0.3	4.0	6.8

The Canadian Official Grain Grading Guide for wheat (August 1, 2015) categorized several grades of wheat based on test weight, i.e. the number of kg per hectoliter (hl). For example, the Canadian Western Red Spring wheat (CWRS) belonging to Grade 1 should have a minimum of 79 kg/hl, Grade 2 minimum 77.5 and Grade 3 minimum 76.5 kg/hl. It means that the difference between Grade 1 and Grade 2 is 1.5 kg/hl,

while the difference between Grade 1 and Grade 3 is 2.5 kg/hl only. It is obvious that the DE concentration of only 100 ppm already reduced test weight for 4 kg and, if Grade 1 contained a minimum 79 kg/hl, the application of DE at 100 ppm would move that grain from Grade 1 to Grade 3. The reduction in price from Grade 1 to Grade 3 wheat is significant. This is the main reason why the grain industry refuses to use DEs for direct mixing with grains.

### 1.2.3 Differences in insect species tolerance to the same DE formulation

In the last decade, many papers were published in various scientific journals dealing with research of the effectiveness of various DEs against several stored product insect pests. Although different and often completely contradictory results were reported, there is a general conclusion that can be made about the sensitivity of stored-product insects to DE. Given the same commodity, there was a significant variation in the susceptibility of different insect species to the DE Protect-It. The insects, in the order of most-to-least susceptible were: *Cryptolestes ferrugineus* Steph., rusty grain beetle; *Oryzaephilus surinamensis* L., sawtoothed grain beetle; *Sitophilus oryzae* L., rice weevil; *Sitophilus granarius* L., granary weevil; *Ryzoperthe dominica* F., lesser grain borer; *Tribolium castaneum* Herbst., red flour beetle; and *Prostephanus truncates* (Horn), larger grain borer. The concentrations required to achieve a 90% reduction in offspring were similar, or in some cases significantly higher than the concentrations required to reduce parent populations 90% (Maceljski & Korunic, 1972; Desmarchelier & Dines, 1987; Fields & Muir, 1996; Korunic, 2007b; Korunic & Fields, 2006).

The difference in tolerance even among the species of the same genus is considerable (Table 3).

**Table 3.** The LD<sub>50</sub> and LD<sub>90</sub>, and 95% confidence interval of *S. zeamais*, *S. oryzae* and *S. granarius* adults held on wheat treated with Diafil 610 or Celatom MN 23 diatomaceous earths after 21 days (Korunic & Fields, 2006)

Diatomaceous earth	Insect	LD <sub>50</sub>	95% CL	LD <sub>90</sub>	95% CL
Diafil 610	<i>S. zeamais</i>	232	213 - 248	418	391 - 452
	<i>S. oryzae</i>	547	503 - 585	794	736 - 883
	<i>S. granarius</i>	926	881 - 984	*	*
Celatom MN 23	<i>S. zeamais</i>	211	-	353	-
	<i>S. oryzae</i>	421	394 - 448	700	653 - 759
	<i>S. granarius</i>	776	705 - 869	*	*

\*greater than 1000 ppm

**Table 4.** The efficacy of different diatomaceous earths (DE) on stored wheat treated against rice weevil (RW) and red flour beetle (RFB) (Korunic, 1998)

Insect species	DE	Duration of exposure (days)	LC <sub>50</sub> (95% CI) ppm	LC <sub>90</sub> (95% CI) ppm
Rice weevil	Celite 209 (USA)	5	270 (213-340)	565 (395-857)
	Perma Guard (USA)	5	680 (555-832)	1475 (972-1394)
Red flour beetle	Celite 209 (USA)	14	417 (328-529)	776 (553-1150)
	Perma Guard (USA)	14	1000 ppm = 43%	1000 ppm = 43%

Temperature: 25 °C; r.h.: 55%; m.c. of Hard Red Spring wheat: 14%.

**Table 5.** The mortality of *Sitophilus oryzae*, held at various temperatures and grain moisture conditions, in wheat treated with different diatomaceous earths for five days at 400 ppm (Fields & Korunic 2000)

DE formulations	Temperature and grain moisture			
	Mortality (%) at 20°C		Mortality (%) at 30°C	
	12% m.c.*	14% m.c.	12% m.c.	14% m.c.
Dryacide	78 ± 10	15 ± 4	96 ± 1	33 ± 7
Insecto	74 ± 6	29 ± 5	96 ± 7	32 ± 6
Perma Guard	29 ± 3	7 ± 1	77 ± 6	12 ± 1
Untreated	2 ± 2	0 ± 0	17 ± 7	2 ± 1

\*m.c. – moisture content

Given the same insect species, there was a significant variation in the susceptibility of insect species to various DEs (Table 4). To control the same insect species at the LD<sub>95</sub>, one DE (Celite 209) required 565 ppm, and another DE (Perma Guard) 1475 ppm. This is really a very big difference (2.6 times) in concentrations needed to control 95% of a population of the same insect species.

#### 1.2.4 Effects of grain moisture and temperature on effectiveness against insects

It is well-known that the mode of action of DE is through insect desiccation (Carlson & Ball, 1962; Maceljski & Korunic, 1972; La Hue, 1978; Desmarchelier & Dines, 1987; Aldryhim, 1990, 1993).

An increase in the moisture content of treated grain will considerably reduce the efficacy of a DE, especially if moisture

content is more than 14% or relative humidity exceeds 70% (Korunic, 1994). It means that products with high moisture content should not be treated with DE or, having no other solution, that increased dosages should be applied. Higher temperature increases the efficacy of DE with an exception of species of the genus *Tribolium* (*T. castaneum* and *T. confusum*), which show greater tolerance at 30 °C than at 22-24°C (Maceljski & Korunic, 1972; Aldryhim, 1990).

Some of our research results on the effects of grain moisture and temperature on DE efficacy against *Sitophilus oryzae* are presented in Table 5. The results show clearly that an increase in grain moisture content of 2% (from 12 to 14%) significantly decreased the efficacy of several DEs. Conversely, a temperature increase from 20°C to 30°C significantly increased their effectiveness against *S. oryzae*.

These results support an opinion that grain moisture and temperature are very important and somewhat limiting for an effective use of DEs in grain protection.

**Table 6.** The influence of various commodities on the efficacy of DE Protect-It against *Sitophilus oryzae* (RW) at 300 ppm (Korunic, 2007b)

Commodity	Class	Grade	Moisture content %	Adult RW mortality (%) after 21 days
Wheat	Ontario soft wheat	2	14.3	46±13
	Hard Red Spring	2	14.0	85±17
Corn	With 7.8% oil	1	13.3	23±22
	With 4.4% oil	1	13.3	10±5
Rice	Milled	N/A	13.0	2±3
	Paddy	N/A	13.0	100±0

### 1.2.5 Influence of various commodities on the efficacy of DEs

Studying the efficacy of DEs on different wheat classes, Aldryhim (1990) detected a significant variation in their efficacy against the same insect species. The efficacy of silica dust Dryacide against *Rhizopertha dominica* was highly influenced by wheat class.

The effect of different types of commodities (rice, sorghum, rye, corn, wheat) and different classes and grades of wheat on the efficacy of diatomaceous earth was investigated (Korunic, 2007b). There were significant differences in the efficacy of the same DE against *Sitophilus oryzae* (L.) adults and their progeny on different types of commodities and on various classes of wheat. After an exposure time of 21 days, the mortality of *S. oryzae* on milled rice and corn caused by 300 parts per million (ppm) of the enhanced diatomaceous earth Protect-It was not significantly different from the mortality observed on untreated corn and rice. However, *S. oryzae* mortality on Hard Red Spring wheat was 85%, and 100% on treated paddy rice (Table 6).

These very high differences in the efficacy of DE applied to different commodities are considerable disadvantages of DEs, considering the resulting need to study the effectiveness of each DE on different commodities to determine their effective concentrations on each type of commodity and each insect species.

### 1.2.6 Use of DEs in some other fields

Research has also focused on the effects of DEs on numerous other insects, such as ants, bedbugs, fleas, centipedes, pill-bugs, ticks, crickets, termites, earwigs, silverfish, textile pests (Pest Control field), various caterpillars in agriculture, June beetles, potato beetles, snails, as well as poultry mites, etc. (Wilbur et al. 1971; De Crosta, 1979; Snetsinger, 1982, 1988; Schultz et al., 2014). Different DE formulations are currently used to a certain extent to control these pests.

### 1.3 POSSIBLE SOLUTIONS FOR OVERCOMING OBSTACLES TO DIRECT MIXING OF DE WITH GRAINS

Many research papers have been published so far in international scientific journals trying to discover new ways of using DEs and thus to continue the utilization of this safe and chemically inert dust. In order to reduce DE dosages that have adverse effect on grain quality, DE is often mixed with other compounds, such as silica gel, dry honey, not activated yeast and sugar to increase its efficacy. Some DE mixtures are already on the market: DE plus pyrethrins, DE plus yeast and sugar, DE plus silica gel (Quarles & Winn, 1996; Korunic & Fields, 1995; Subramanyam & Roesli, 2000; Korunic et al., 2015). However, these mixtures have to be effective at rather high dosages, which still have a significant negative effect on grain bulk density and flowability (Jackson & Webley, 1994; Korunic et al., 1998). One of possible solutions to the implications caused by high doses of DEs is a combined use of DE with other reduced-risk methods with insecticidal activity, such as extreme temperatures (Fields et al., 1997; Dowdy, 1999), grain cooling with a surface treatment with DE (Nickson et al., 1994), or in a mixture with entomopathogenic fungi (Lord, 2001; Akbar et al., 2004; Kavallieratos et al., 2006; Vassilakos et al., 2006; Michalaki et al., 2007), in a mixture with reduced concentrations of synthetic insecticides (Korunic, 2001; Stathers, 2003; Arthur, 2004; Athanassiou, 2006; Chanbang et al., 2007; Korunic & Rozman, 2010) or in a mixture with plant extracts (Korunic, 2007a; Athanassiou & Korunic, 2007) or in a mixture with bacterial metabolites (Vayias et al., 2009; Vayias & Vassiliki, 2009). Experimentation with other components has often revealed enhanced and sometimes synergistic effectiveness (Korunic, 2001; Lord, 2001; Stathers, 2003; Korunic, 2007a; Athanassiou & Korunic, 2007; Athanassiou et al.,

2008; Korunic & Rozman, 2010). However, these mixtures still contained rather high concentrations of DE with significant reducing effects on bulk density and flowability. The exemptions were mixtures of DE with synthetic insecticides using low DE concentrations, but these formulations were less safe for their applicators and consumers.

Arnaud et al. (2005) suggested that a new DE formulation be developed which could be more effective at a low dose rate. This could be achieved by blending together DE formulations with good efficacy. With such a blend it would be possible to take advantage of several DEs in one formulation, e.g. good desiccation power of one DE, excellent abrasive properties of another and small particle size of a third DE.

Athanassiou et al. (2007) studied the effectiveness of a mixture of three DEs: Insecto, Pyrisec and Protect-It. Their results clearly showed that a blending of several DEs together may produce a new DE formulation. However, the authors described the composition of these 3 formulations and it was obvious that their experiments were not conducted with pure natural DEs. Insecto contains 10% of food grade bait, Pyrisec 1.2% of pyrethrin, and Protect-It contains 10% of synthetic silica gel. The effect of the added materials in the formulations is not known.

Korunic (results not published yet) has studied 6 different DE formulations, and their mixtures (15 mixtures) against insects. Some of the formulations are very effective, while others have low effectiveness against insects. The results are not in agreement with an opinion of Arnaud et al. (2005) and results reported by Athanassiou et al. (2007) because the mixtures in our experiments did not generate higher effectiveness. We suppose that mixing different DEs could not be considered as one of the possible solution to overcome DE limitations in use.

Another possibility to overcome the obstacles to DEs use for grain protection is combining the most effective DEs with other natural insecticides with different modes of action against insects, i.e. desiccation of insects caused by a DE with toxicity against insects caused by another substances (Korunic, 2001; Korunic 2007a, Athanassiou & Korunic, 2007). In many cases, the synergy between DE and another substance(s) greatly enhanced the effectiveness of their mixture and the required effective DE doses were therefore reduced approximately 4-10 times in comparison with DE doses used alone (Korunic, 2007a; Athanassiou & Korunic, 2007; Almasi et al., 2013).

## 1.4 CONCLUSIONS

DE is still not in widespread commercial use for direct mixing with grains intended for the market because of several major obstacles and disadvantages as a grain protectant. The main obstacles are: its unacceptable effect on grain flowability, the effect on bulk density or test weight, i.e. shifting grains to lower grain grades, different tolerance of insect species to DEs, significant effects of grain moisture and temperature on DE effectiveness, and significant effect of different commodities on DE effectiveness against insects. Because of all these significant and unacceptable obstacles to in direct mixing of DEs with grains, it is quite clear that DE as grain protectants have only a minimal chance, if any, to be accepted by the grain industry. However, DEs may have a wider application on farms to protect grains for own use and for structural treatments (various surfaces) in grain and food industry.

Therefore, it is very important to continue work on developing a safe enhanced formulation with a low concentration of DE and minimal adverse effect on bulk density and grain flowability. If this newer enhanced formulation can respond to the limitations of diatomaceous earth use for direct mixing with grains, there will be a wider acceptance of diatomaceous earth as a means to control stored-product insect pests.

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## Pregled nepoželjnih efekata prilikom mešanja dijatomejske zemlje sa žitom

### REZIME

Unatoč brojnim prednostima uporabe dijatomejske zemlje (DZ) i prihvatljive djelotvornosti na smrtnost insekata, ali zbog njezinog velikog utjecaja na smanjenje hektolitarske mase i sipkavost zrnene robe primjena za izravno mješanje s robom je jako ograničena. U radu se opisuju glavni nedostaci uporabe DZ za izravno mješanje sa zrenom robom poput zdravstvenog rizika, smanjenje hektolitarske mase, razlike u osjetljivosti insekata na DZ, utjecaj vlage i temperature zrna na efikasnost, utjecaj različite vrste zrnene robe na efikasnost te uporaba DE u drugim područjima. Zbog velikih neželjenih utjecaja DZ na kvalitetu robe istražuju se mogućnosti razvoja novih DZ formulacija s povišenom djelotvornosti na insekte uporabom sniženih doza za izravno miješanje sa zrenom robom. Ako te nove formulacije mogu smanjiti negativni utjecaj DZ postoji stvarna mogućnost za povećanu primjenu DZ u praksi.

**Ključne reči:** Dijatomejske zemlje; Uskladišteni proizvodi; Žito; Suzbijanje štetnih organizama