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Efficacy of Various Chemicals as Grain Mold Inhibitors

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ABSTRACT

Of various organic acids and related compounds, propionic acid was the most effective and consistent as a mold inhibitor for corn and grain sorghum at moisture contents of 18-24 percent. Isobutyric, acetic, and formic acids followed in order. Salts of acids were less effective. Sorbic acid was effective when in solution.

INTRODUCTION

Early harvesting of fall grains at high moisture contents has certain advantages: yields are higher because field losses are lower, farmers are less likely to be bothered by bad weather and there is more time for other fall field work. In terms of feed efficiency and/or rate of gain, high-moisture grain is generally superior to dry grain as a livestock feed.

There has been considerable interest recently in methods of storage which take advantage of high-moisture harvesting and high-moisture feeding without drying the grain for storage. The two principal storage methods for high-moisture grain are ensiling, or sealed storage, and the use of mold-inhibiting chemicals. This paper deals with the second method, and specifically, with the relative effectiveness of various chemicals we have tested as grain preservatives. Previous work has been concerned primarily with two organic acids, acetic and propionic (Campbell 1972, Christensen 1973 and Sauer et al. 1972).

To be useful as a mold inhibitor, a chemical must have several attributes: (a) prevent spoilage and deterioration over a wide range of moisture and temperature conditions at application rates which are economically competitive; (b) produce no problems of toxicity or palatability in livestock; (c) be reasonably safe to handle and require a minimum of special equipment for application and storage. The materials used in the tests described here were thought to be among the most likely to meet these criteria.

MATERIALS AND METHODS*

Corn and grain sorghum were adjusted to the required moisture levels (18 to 24 percent) by adding water and mixing intermittently until moisture was satisfactorily equilibrated. This process required from several hours to overnight, depending on the amount of water added. Chemicals were added directly to the grain in a container of appropriate size and then shaken or mixed to distribute the material. Treatment rates are expressed as percentages on a w/w basis for dry chemicals and v/w for liquids. Attempts to spray or atomize liguids onto the grain resulted in too much loss to the atmosphere.

Because many of the chemicals used are corrosive, laboratory incubators or controlled-environment chambers were not used. Instead grain was stored at room temperature in 1.5-mil polyethylene bags. This method of storage permits adequate exchange of oxygen and CO_2 for mold growth, yet maintains the original moisture content (MC) of the grain for several months. Insofar as possible, the grain was kept in the dark during storage to lessen the amount of light-catalyzed lipid degradation.

Grain was observed visually during storage for signs of mold growth and was tested periodically for moisture content and the presence of internal fungi. Moisture content of corn was determined by drying 20 g of whole corn 72 hr in a forced-draft oven at 103 C (AACC, 1962). Whole sorghum grain was dried 17 hr at 120 C. This method agreed closely with the standard two-stage air-oven method (AACC, 1962) over a wide range of moisture contents, and was much more convenient. All moisture contents are given on a wet weight basis. The presence of internal fungi was determined by washing 100 kernels in 2 percent NaOCl for 1 min, rinsing in sterile water, and placing on Difco malt agar containing 4 percent NaCl and 200 ppm Tergitol NPX (Union Carbide Corp.). After incubating 5 to 7 days at 25 C, fungi were identified and counted.

RESULTS AND DISCUSSION

Test 1: Corn adjusted to 18, 20 and 22 percent MC and treated with 0.5 and 1.0 percent of various chemicals.

Yellow corn with 11.5 percent MC was adjusted to approximately 18, 20 and 22 percent MC and stored at approximately 27 C. Table 1 shows the degree of mold prevention achieved by the various treatments. In this and subsequent tests the grain was considered no longer relatively mold-free when more than 10 percent of the kernels became internally invaded by storage molds.

This degree of invasion was some-

TABLE 1. MOLD-FREE STORAGE TIME (WEEKS) FOR CORN WITH 18, 20, AND 22 PERCENT MOISTURE CONTENT STORED AT APPROXIMATELY 27 C

Chemical applied	0.5% application rate			1.0 % application rate		
	18%MC	20%MC	22%MC	18%MC	20 %MC	22%MC
None	less than one week			less than one week		
Potassium sorbate	2	1	1	3	2	1
Sorbic acid	7	2	1	12	5	1
Calcium propionate	1	4	0	1	10	10
Sodium propionate	17+	5	3	17+	17+	17+
Acetic acid (glacial)	17+	17+	7	17+	17+	12
Propionic acid	17+	17+	17+	17+	17+	17+

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TABLE 2. MOLD-FREE STORAGE TIME (WEEKS) FOR SORGHUM WITH 19, 21, AND 22 PERCENT MOISTURE CONTENT STORED AT APPROXIMATELY 27 C

Chemical applied	0.5% application rate			1.0% application rate		
	19%MC	21%MC	22%MC	19%MC	21%MC	22%MC
None	less than one week			less than one week		
Potassium sorbate	1	0	0	2	1	1
Sorbic acid	2	1	1	5	2	1
Calcium propionate	0	0	0	0	0	0
Sodium propionate	0	1	0	10	5	12
Acetic acid (glacial)	4	1	2	12+	8	8
Propionic acid	16+	16+	16+	16+	16+	16+

times difficult to determine precisely because of a slow decline in original microflora and a simultaneous increase in storage molds. The propionate salts in particular are relatively slow in killing original fungi, so that after 1 week fungi may have been numerous, but in 2 weeks they were either very scarce or very abundant depending on whether the treatment rate was adequate or not. The free acids such as acetic and propionic were much more effective in eliminating original microflora, so results were easier to interpret. Potassium sorbate was the least effective, with sorbic acid and calcium propionate also relatively ineffective. The results with calcium propionate were somewhat anomalous in that the treatments failed completely at 18 percent MC whereas they had more effect at higher moistures. Sodium propionate followed the more normal pattern of being most effective at lower moisture levels. A possible explantion for this difference is that the salts are activated by contact with water, and 18 percent moisture was not enough to dissolve the calcium salt. Sodium propionate is very hygroscopic and deliquescent, but calcium propionate is not.

The principal fungi which grew in grain without adequate treatment were *Aspergillus glaucus, A. candidus,* and *Penicillium* spp. at 18 percent MC. The same fungi plus *A. flavus* and *A. niger* grew at 20 percent MC; *Mucor* spp., *Fusarium* spp., *Monascus* sp., and *A. Versicolor,* in addition to the previous list, were commonly found at 22 percent MC.

Test 2: Grain sorghum adjusted to 19, 21 and 22 percent MC and treated with 0.5 and 1.0 percent of various chemicals.

Sorghum with 12.5 percent initial MC was adjusted to 19, 21 and 22 percent MC and treated the same as the corn in Test 1. The length of time various treatments prevented mold growth are shown in Table 2.

Propionic acid was clearly the most effective chemical, with the others generally less effective than on corn in Test 1. The sorghum, obtained from a commercial elevator, had unusually high initial populations of a great variety of fungi. This, along with slightly higher moisture contents, made the storage test more severe. As in the previous test, the propionate salts were not very consistent in their activity, but the sodium salt was more effective than the calcium salt. The fungi which grew in sorghum that was inadequately treated were generally the same as those in corn. However, there were more species present in any given sample compared to the corn, and the list of common species also included *Aspergillus ochraceus, A. terreus,* and yeasts.

Test 3: Corn treated with various chemicals and stored at 22 percent MC and 23 C.

Yellow corn with 13.5 percent MC was adjusted to 22 percent MC and treated as follows: Three-kilogram lots of grain were treated with different amounts of various chemicals (Table 3) each diluted with 6 ml of distilled water to facilitate spreading the material on the corn. Exceptions were sorbic acid, which was applied as a 10 percent solution in absolute ethanol, and the two mixtures containing sorbic acid. Sorbic acid is not water soluble. After treatment, each lot was divided into two 1500-g portions for storage. Propionic acid was a very effective mold inhibitor and was far superior to acetic and formic acids. Combinations of formic:acetic, formic:propionic, or acetic:propionic acid were less effective than straight propionic acid, and generally appeared to have an activity intermediate between those of the separate acids involved.

The unexpected result in this test was the high mold-inhibiting activity of sorbic acid (Table 3). In Tests 1 and 2, sorbic acid was very ineffective when applied as a dry powder. It was much more effective applied as a solution. Acetic acid containing 10 percent sorbic acid was approximately twice as effective as acetic acid alone. Sorbic acid dissolved in ethanol was extremely effective. In Table 3, 0.2 percent sorbic acid was actually a 2 percent application of 10 percent sorbic acid. Half that amount (not shown in the table) was also effective. Although a control treatment with ethanol alone was not included in this test, earlier observations had indicated that comparable amounts of ethanol alone were not effective as grain mold inhibitors. Sorbic acid is more expensive than propionic acid and its relative insolubility in water may create problems in application, but results of this test indicate that it warrants further testing and evaluation.

Test 4: Corn adjusted to 19 percent MC, treated with chemicals and stored at 23 C.

This test compared four closely related acids: formic, acetic, propionic, and isobutyric. These acids contain one to four carbon atoms, respectively. Because ammoniun isobutyrate is of current interest commercially and because ammonia itself has received consideration as a mold inhibitor, ammonium salts of acetic and isobutyric acid were included. A non-corrosive derivative of

TABLE 3. MOLD-FREE STORAGE TIME (WEEKS) FOR CORN WITH 22 PERCENT MOISTURE CONTENT STORED AT APPROXIMATELY 23 C

Chemical applied	Application rate 0.2%	0.3%	0.4%	0.6%
None	less than one week			
Formic acid	1		2	35+
50% Formic:50% acetic	1		2-3	*
Acetic acid (glacial)	2-3		5	35+
60% Acetic:40% propionic	3	4-5	7	35+
50% Formic:50% propionic	3		35+	
70% Acetic:20% propionic:10% sorbic	4	8-9	35+	
90% Acetic:10% sorbic	5	8-10	35+	
Propionic acid	6	10-15	35+	
Sorbic acid in ethanol (2% application of 10% solution)	35+			

* Corn infested by mites after 17-22 weeks

TABLE 4. MOLD-FREE STORAGE TIME (WEEKS) FOR CORN WITH 19 PERCENT MOISTURE CONTENT STORED AT APPROXIMATELY 23 C

Chemical applied	Application rate 0.2%	0.3%	0.4%
None	1	1	1
Ammonium acetate	1	1	1
Formic acid	2	3-5	6-9
Acetic acid (glacial)	3-6	6-7	8-9
Ammonium isobutyrate	3	7-8	9
Isobutyric acid	8	10-11	12-19
Propionic acid	10-17	22+	22+
Methylene bis propionate	22+	22+	22+

TABLE 5. MOLD-FREE STORAGE TIME (WEEKS) FOR CORN WITH 24 PERCENT MOISTURE CONTENT STORED AT APPROXIMATELY 23 C

Chemical applied	Application rate 0.3%	0.4%	0.5%
None		less than one week	
Ammonium acetate	0	0	0
20% Propionic:80% acetic	0	0	2
Formic acid	1	1	2
Acetic acid (glacial)	1	1	2
Ammonium isobutyrate	1	2	2
50% Propionic:50% acetic	0	2-3	4-6
Formic-isobutyric mixtures	1	2	4-7
20% Propionic: 80% formic	1	3	7-8
20% Propionic:80% isobutyric	0	2	8-9
50% Propionic:50% isobutyric	1	1-4	9
Isobutyric acid	1	2	9
50% Propionic:50% isobutyric	1	6-7	22+
80% Propionic:20% acetic	2	8-9	22+
80% Propionic:20% isobutyric	3	6-8	22+
80% Propionic:20% formic	3	7-9	22+
Propionic acid	8	22+	22+
Methylene bis propionate	10-15	22+	22+

propionic acid, methylene bis propionate (Chevron Chemical Co.) also was tested.

Chemicals were applied as 50 percent aqueous solutions to 3000-g lots of grain, except for methylene bis propionate, which is not water soluble. Isobutyric acid, which is only slightly water soluble, was mixed 50 percent with water, shaken vigorously, and the resulting temporary emulsion or suspension applied to the corn. Ammonium isobutyrate also was tested in its dry powdered form. After treatment, duplicate 1500-g portions were stored at 23 C.

Table 4 shows that ammonium acetate was completely ineffective, and formic acid was somewhat inferior to acetic acid and ammonium isobutyrate. The latter compound was equally effective as a powder or a solution. Methylene bis propionate was somewhat superior to propionic and isobutyric acids. The suitability of methylene bis propionate as a mold inhibitor will depend on its effects on animals and its cost relative to the acids. In corn where fungi developed, *Aspergillus glaucus* and *Monascus* sp. were the principal species. *A. flavus* grew in formic acid-treated grain, and untreated grain was invaded by a great variety of fungi.

Test 5: Corn adjusted to 24 percent MC, treated with chemicals, and stored at 23 C.

Chemical treatments were the same as in Test 4 plus various binary mixtures of acids. Formic, acetic, and isobutyric acids were mixed with propionic in ratios of 80:20, 50:50, and 20:80. The same ratios of formic-isobutyric acid mixtures also were tested. Reports from several chemical companies indicated that their own research showed a synergistic effect when two or more acids were combined as a mold inhibitor.

The results summarized in Table 5 do not show anything more than a purely additive effect from the various organic acid mixtures, with those mixtures high in propionic acid being most effective. A possible exception is that formic-propionic mixtures were somewhat better than formic-acetic mixtures. Formic acid alone was equal to acetic acid in this test.

As in Test 4, methylene bis propionate was somewhat superior to propionic acid. The principal fungus which grew in inadequately treated corn was *Monascus* sp. Yeasts also were found, and *Aspergillus flavus* was common in formic acid treatments.

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