METHOD OF CONTROLLING WEEDS PRE-EMERGENTLY

6 Claims, No Drawings

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Field of Search 71/92

References Cited

UNITED STATES PATENTS


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CLAIM: 1. A method of eliminating weeds from an area infested with weed seeds and growing weeds which comprises contacting said area with an effective amount of a benzimidazole represented by the formula

\[
\text{R}^+ \text{R}^- \text{R}^+ \text{N} \quad \text{C} \quad \text{R}^-
\]

wherein \(R\) is a perfluoro \(C_1-C_3\) alkyl group and \(R'\), \(R''\), \(R'''\) and \(R''''\) are the same or different members of the group consisting of hydrogen, halo, nitro, \(C_1-C_2\) alkyl, \(C_1-C_2\) alkoxy and trifluoromethyl.
METHOD OF CONTROLLING WEEDS PRE-EMERGENTLY

This invention relates to a novel herbicidal process comprising the application to an area infested with weed seeds and which is to be planted to crops, of a herbicidal amount of a benzimidazole represented by the formula:

wherein R is a perfluoro C₄-C₆ alkyl group; R' and R" are either hydrogen, halo having an atomic number less than 82, nitro, C₆-C₁₂ alkoxy or trifluoromethyl; and R‴ and R‴ are either hydrogen, halo having an atomic number less than 82, nitro, C₆-C₁₂ alkoxy, trifluoromethyl or C₁₂-C₂₅ alkyl.

Substituted benzimidazoles corresponding to the above formula which are substituted in the benzene ring portion of the molecule are named for convenience according to the numbering system above; that is to say, a single substituent on one of the two carbon atoms adjacent to the benzimidazole ring portion will be called a 4-substituent and a single substituent on one of the two carbon atoms remote from the benzimidazole ring portion will be called a 5-substituent. As will be apparent to those skilled in the art, however, the imidazole ring exists as an equilibrium mixture of two tautomeric forms inasmuch as the hydrogens of the imidazole ring can shift from one of the nitrogens to the other. For example, a 4-halobenzimidazole can also be named as a 5,7-dichlorobenzimidazole and the compound, as it actually exists, is a mixture of these two tautomers. It should be understood, therefore, that the alternate tautomeric structure is in every instance intended to be disclosed by the naming system used throughout this specification.

Compounds coming within the scope of the above formula include the following:

2,4,7-tris(trifluoromethyl)benzimidazole
2,4,6-tris(trifluoromethyl)benzimidazole
4,5,7-trichloro-2-trifluoromethylbenzimidazole
2-trifluoromethyl-5-fluorobenzimidazole
4-nitro-6-chloro-2-pentafluorothienobenzimidazole
4-fluoro-2-trifluoromethylbenzimidazole
4-chloro-2-trifluoromethylbenzimidazole
4-fluoro-7-chloro-2-pentafluorothienobenzimidazole
6-methyl-5,7-dichloro-2-trifluorobenzimidazole
4-chloro-7-n-propoxy-2-pentafluorobenzimidazole
4,5-dimethoxy-2-trifluoromethylbenzimidazole
4-bromo-2-trifluorobenzimidazole
4,7-dinitro-2-heptafluorobenzimidazole
4-nitro-6-fluoro-2-heptafluoropropylbenzimidazole
5-ethoxy-6-methyl-2-trifluorobenzimidazole
4-nitro-5-ethoxy-2-pentafluorothienobenzimidazole and the like.

According to my novel process, a compound represented by the above structure is applied in a suitable formulation at the rate of from 0.5 to 8 pounds per acre to an area which is to be seeded to a crop plant such as corn, cotton or soybeans, which area contains, in addition, weed seeds belonging to both monocotyledonous and dicotyledonous weed species; i.e., the herbicidal benzimidazole is applied preemergently to both crops and weeds. For application to a particular area, the trifluorobenzimidazole can be formulated as a wettable powder, as a liquid emulsion, or in solid form as a dispersion on a solid carrier.

In a typical demonstration of the use of one of the compounds coming within the scope of the above formula as a pre-emergent herbicide, 2,5-bis(trifluoromethyl)benzimidazole was formulated as a 25 percent wettable powder, the other ingredients of the formulation being kaolin, a surfactant such as the sodium salt of a naphthylenic sulfonic acid, and a dispersant, such as the sodium salt of sulfonated lignin. This wettable powder was dissolved in 500 ml. of water, and the resulting solution was placed in the concentrate tank of a logarithmic sprayer. A sufficient quantity of 2,5-bis(trifluoromethyl)benzimidazole was used to give an initial application rate of 8 pounds per acre as the sprayer was calibrated to deliver spray at the rate of 30 gallons per acre. The sprayer was set so that the dosage rate was halved every 6.6 feet of sprayer travel. Stated another way, the spray was applied in an amount that decreased logarithmically from the initial application rate of 8 pounds (30 gallons) per acre as the sprayer moved forward, the half-dosage distance (the distance at which the rate delivered was one-half that of each of the original rates) being 6.6 feet. A 6-foot-wide band 19.8 feet long was then sprayed with the herbicidal benzimidazole.

In that distance, three half-dosage intervals were obtained, beginning with a dosage rate of 8 pounds of the benzimidazole per acre and ending with a dosage rate of 1 pound per acre. A similar control area was sprayed using only the emulsion medium without any added herbicidal compound. In the plot thus treated, a 2-foot-wide band was soil incorporated along the long axis of the plot. Weed counts were obtained by counting the number of weeds in each variety in 2-square-foot areas in both the treated and untreated plots. In addition, at each half-dosage interval (at 4, 2, and 1 pounds per acre dosages), crop injury ratings were also made in two square-foot areas. Table I which follows gives the results of this trial. In the table, column 1 gives the application rate, column 2, the percent control of grass weeds, column 3, percent control of pigweed, column 4, percent control of other susceptible broadleaf weeds, including purslane, lambs-quarter, smartweed and cartwetew, column 5, the percent of resistant broadleaf weeds, including ragweed, Venice mallow and velvetleaf.

<table>
<thead>
<tr>
<th>Rate</th>
<th>Grass Weeds</th>
<th>Pigweed</th>
<th>Other Weeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 lb/acre</td>
<td>95</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>4 lb/acre</td>
<td>84</td>
<td>88</td>
<td>76</td>
</tr>
<tr>
<td>2 lb/acre</td>
<td>81</td>
<td>42</td>
<td>51</td>
</tr>
<tr>
<td>1 lb/acre</td>
<td>73</td>
<td>67</td>
<td>76</td>
</tr>
</tbody>
</table>

There was no injury to either soybeans or corn at application rates varying from 1 to 8 pounds per acre. There was moderate damage to oats at application rates of from 2 to 6 pounds per acre, but none at 1 pound per acre. The injury to the grass weeds was severe at dosages of 2 to 8 pounds per acre, and the injury to pigweed was severe at 8 pounds per acre with slight to moderate injury at 2 to 4 pounds per acre. Other weeds showed little or no injury despite the fact that the number of these weeds were reduced over that in the control group. Soil incorporation did not seem to affect the percent control appreciably in the treated plots, although it did seem to increase the weed damage at high-application rates.

In addition to the field testing of the process of this invention as exemplified above by the use in the field of 2,5-bis(trifluoromethyl)benzimidazole, the unusually high ability of other compounds included within the scope of the above formula to perform as effective preemergent herbicides has been demonstrated in the greenhouse. For example, 2-trifluorobenzimidazole applied preemergently to both weeds and crops at an application rate of 8 pounds per acre either kills or severely affects the growth of large crabgrass,
mustard, pigweed and foxtail without affecting in any way the growth of corn, cotton, or soybeans. Similarly, 5-chloro-2-trifluoromethylbenzimidazole, at an application rate of 8 pounds per acre, kills or severely affects the growth of the weed species used in the test: large crabgrass, pigweed, foxtail and velvetleaf, without affecting adversely the growth of the three crop plants. 5-Fluoro-2-trifluoromethylbenzimidazole acts similarly at an application rate of 4 pounds per acre and 5,6-dichloro-2-trifluoromethylbenzimidazole is similarly effective at an application rate of 2 pounds per acre. As is usual with preemergent herbicides, the more effective compounds will show minimal crop damage at very high preemergent application rates. Nevertheless, these more effective compounds severely damage or kill weed species at application rates one-fourth to one-eighth that at which any crop damage can be demonstrated. For example, 5-chloro-2-trifluoromethylbenzimidazole shows some minimal crop damage when applied preemergently to both crops and weeds at an application rate of 8 pounds per acre, at which rate it kills all the usual weed species. However, at 4 pounds per acre, the crops grow without any appreciable effect caused by the application of the benzimidazole while the same weed species are either killed or their growth severely affected. With each of the compounds represented by the above formula, there is a preemergent application rate at which they will either kill or severely damage grass weeds and susceptible broadleaf weeds without in any way injuring crop plants such as corn, cotton, or soybeans.

The herbicidal processes of this invention customarily employ a compound represented by the above formula in the form of a dispersion. Such dispersion can be applied in liquid form by spraying or in solid form by using a fertilizer applicator or the like. Formulations suitable for spraying can be prepared as emulsifiable concentrates or wettable powders. Typical useful formulations include the following:

1. Liquid Formulation
   60 mg. of 5-chloro-2-trifluoromethylbenzimidazole
   1.25 ml. of ethanol
   12.5 ml. of water
   0.0125 ml. of dispersant

Useful dispersants for the above formulation include a mixture of the calcium salt of benzene dodecylsulfonate and either a polyoxyethylene ether of nonylphenol containing 9 ethylenoxide residues in the polyoxyethylene chain or a polyoxyethylene-sorbitan mono-oleate.

2. Solid Formulation
   25 grams of 5-fluoro-2-trifluoromethylbenzimidazole
   70.5 grams of kaolin
   1.5 grams of sodium lignin sulfonate
   3 grams of a polyoxyethylene ether of nonylphenol containing 9 ethylenoxide residues in the polyoxyethylene chain.

In addition to their selective preemergence activity, the compounds represented by the above formula are also useful as all-purpose postemergent herbicides, with many of the compounds showing a marked ability to virtually eliminate weeds and crop plants at application rates varying from 2 to 8 pounds per acre depending upon the particular compounds. Because of the extremely high postemergent activity of the compounds represented by the above formula and the corresponding lack of herbicidal activity against crop plants preemergent, it is of course possible to employ the compounds in processes which involve applying them preemergent to the crops but postemergent to the weeds. As will be understood by those skilled in the art, however, the opportunities for such selective type of application are strictly limited as compared with applications preemergent to both weeds and crops.

It will be apparent to those skilled in the art that other similar formulations can be prepared using standard techniques.

The compounds utilized in this invention are prepared by the method of Phillips, J. Chem. Soc. 1928, 2, 393. According to this procedure, a suitably substituted o-phenylenediamine and an organic acid are condensed in the presence of a strong acid, usually hydrochloric acid, to yield the desired product. Inasmuch as perfluoroacetic acid has an acid strength equivalent to that of a strong mineral acid, the synthesis of 2-trifluoromethylbenzimidazole and related 2-perfluorooalkylbenzimidazoles represented by the above formula can be accomplished without the addition of a mineral acid. A typical preparation follows:

Example I

5-Chloro-2-trifluoromethylbenzimidazole

A mixture was prepared containing 30 ml. of trifluoroacetic acid and 70 ml. of water. 7.1 grams of p-chloro-o-phenylenediamine were added and the resulting mixture was refluxed for about 4 hours. The reaction product, a heavy black oil containing a few crystals, was poured into water and stirred until the oil solidified. The product was dissolved in base at a pH of about 11 and some black insoluble material was filtered therefrom. The pH was then lowered to about 7 at which point 5-chloro-2-trifluoromethylbenzimidazole began to crystallize out of solution. The product was separated by filtration, the filter cake washed with water, and then dried. Recrystallization from a benzene-hexane solvent mixture yielded 5-chloro-2-trifluoromethylbenzimidazole, melting at about 183°-184°C.

Example II

4-Nitro-2,6-bis(trifluoromethyl)benzimidazole

A solution of 40.5 g. of 2,6-dinitro-4-trifluoromethyl-1-chlorobenzene in 300 ml. of benzene was mixed with 250 ml. of 14 N ammonium hydroxide. The reaction mixture was stirred at room temperature for about 1.5 hours, at which point in time another 100 ml. of 14 N ammonium hydroxide were added and the stirring was continued for an additional 2 hours. The organic layer was separated, was washed with water and was dried. Removal of the solvents in vacuo yielded 2,6-dinitro-4-trifluoromethylaniline, which melted at about 142°-144°C. After recrystallization from a hexane-benzene solvent mixture.

About forty grams of 2,6-dinitro-4-trifluoromethylaniline were dissolved in 300 ml. of ethanol. The solution was heated to about 35°C. and 110 ml. of a 20 percent ammonium polysulfide solution containing 5 percent free sulphur was added. The temperature of the reaction mixture rose spontaneously to about 60°C., at which temperature it was maintained by heating for about 10 minutes. The reaction mixture was cooled to about 40°C. and poured into water. The resulting mixture was filtered. Excess benzene was added to the filtrate which was then evaporated to dryness in vacuo using the water-benzene azoetrope. Recrystallization of the resulting solid yielded purified 3-nitro-5-trifluoromethyl-o-phenylenediamine melting at about 121°-123°C.

Following the procedure of example I, 3 g. of 3-nitro-5-trifluoromethyl-o-phenylenediamine was reacted with 10 ml. of trifluoroacetic acid in 25 ml. of water. 4-Nitro-2,6-bis(trifluoromethyl)benzimidazole formed in the above reaction was isolated by the procedure of example I and melted at about 95°-97°C. after recrystallization from a benzene-hexane solvent mixture.

Example III

4-Nitro-2,6-bis(trifluoromethyl)benzimidazole, thus prepared has a surprisingly high activity as a preemergent herbicide. For example, in greenhouse tests, the compound has demonstrated an ability to eliminate all seedling grass and
Other compounds coming within the scope of this invention have been prepared by Smith and Steinle, J. Am. Chem. Soc., 75, 1,292 (1953), by Belcher, Sykes and Tatlow, J. Chem. Soc., 4,159 (1954), by Fernandez-Bolanos et al., Chem. Soc., 4,003 (1960), and by Bishop et al., Chem. Soc. 3,076 (1964), or are commercially available.

### TABLE II

<table>
<thead>
<tr>
<th>R' R'' R'''</th>
<th>M.P.,°C</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>N</th>
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<tbody>
<tr>
<td>CF₃- H</td>
<td>235-38</td>
<td>36.67</td>
<td>1.8</td>
<td>10.98</td>
<td>37.02</td>
<td>1.73</td>
<td>10.84</td>
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<tr>
<td>CF₃- H</td>
<td>159-30</td>
<td>36.09</td>
<td>2.4</td>
<td>15.00</td>
<td>44.20</td>
<td>2.76</td>
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<tr>
<td>CF₃- H</td>
<td>169-95</td>
<td>41.67</td>
<td>1.74</td>
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<td>36.93</td>
<td>1.29</td>
<td>20.29</td>
<td>34.89</td>
<td>1.69</td>
<td>10.94</td>
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<tr>
<td>CF₃- H</td>
<td>156.2</td>
<td>36.93</td>
<td>1.29</td>
<td>20.29</td>
<td>34.89</td>
<td>1.69</td>
<td>10.94</td>
</tr>
</tbody>
</table>

1 Sub. 2 Not analyzed. Vapor phase chromatography and nuclear magnetic resonance spectrum indicated that the compound had the correct indicated structure.

The following table lists the melting points and analyses of compounds prepared according to the above procedures and believed to be novel:

As will be apparent to those highly skilled in the art, electronegative groups other than those enumerated above for R', R'', R''' and R'''' can be present as substituents in the benzene portion of the imidazole ring, without substantially changing the selective preemergent herbicidal activity characteristic of the disclosed 2-trifluoromethylbenzimidazoles. Included among such electronegative groups are the methylsulfonyl, N-methylsulfonamido, the sulfonamido, the cyano and the like groups.

I claim:

1. A method of eliminating weeds from an area infested with weed seeds and growing weeds which comprises contacting said area with an effective amount of a benzimidazole represented by the formula

   ![Chemical Structure](image)

   wherein R is a perfluoro C₃-C₅ alkyl group and R', R'', R''', R'''', and R'''' are the same or different members of the group consisting of hydrogen, halo, nitro, C₃-C₅ alkyl, C₃-C₅ alkoxy and trifluoromethyl.

2. The process of claim 1 in which the herbicidally active compound is 4-nitro-2,6-bis(trifluoromethyl)benzimidazole.

3. The process of claim 1 in which the herbicidally active compound is 4,5,6,7-tetrachloro-2-trifluoromethylbenzimidazole.

4. The process of claim 1 in which the herbicidally active compound is 5,6-dichloro-2-trifluoromethylbenzimidazole.

5. The process of claim 1 in which the herbicidally active compound is 2,5-bis(trifluoromethyl)benzimidazole.

6. A method to control unwanted plants which comprises bringing into contact with said unwanted plants a herbicidally effective amount of 5-chloro-2-trifluoromethylbenzimidazole.

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