

PATENT SPECIFICATION

(11) 1 268 584

NO DRAWINGS

- (21) Application No. 15533/70 (22) Filed 1 April 1970
 (31) Convention Application No. 812 307 (32) Filed 1 April 1969
 (31) Convention Application 875 507 and 875 508
 (32) Filed 10 Nov. 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 29 March 1972
 (51) International Classification C 07 c 87/62, 91/40; C 07 d 23/06;
 A 01 n 9/20, 9/22; C 07 c 93/14; C 07 d 29/26, 87/38



(52) Index at acceptance

C2C 172—194—284 17X—186—272 183—188—289
 183—193—277 19X—191—270 200 202 220 221
 225 227 22Y 246 250 251 255 25Y 29X 29Y
 311 313 314 31Y 321 322 323 32Y 332 338
 339 360 361 364 36Y 470 471 611 620 630
 631 660 661 694 697 708 791 79Y LP LW MK
 A5E 1A3B 1A3C 1A5B3 1C15A3 1C15A7 1C15B3
 1C15D1 1C15D2 1C15D3 1C7K 1C7P 1C8A

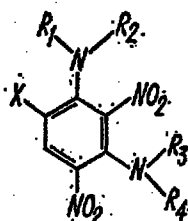
(54) SUBSTITUTED DINITRO-PHENYLENEDIAMINES AND THEIR USE IN HERBICIDAL COMPOSITIONS AND PROCESSES

(71) We, UNITED STATES BORAX AND CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of Nevada, United States of America of 3075 Wilshire Boulevard, Los Angeles, California, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to herbicides.

The invention provides herbicidal compositions and methods of selectively controlling weeds, in which the herbicidally active ingredient is one of a class of substituted dinitrophenylene diamines, most of which are novel compounds. The invention provides also novel, herbicidally active compounds.

The compounds which can be used as herbicides or be the active ingredients of herbicidal compositions according to the present invention are compounds of the formula:—

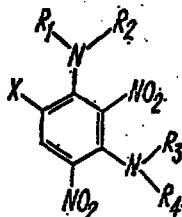


wherein X is a halogen atom or trifluoromethyl group, and each of R₁, R₂, R₃ and R₄ is independently a hydrogen atom or an aliphatic hydrocarbon group which may be substituted by a halogen atom, a hydroxy group or an alkoxy group of 1 to 4 carbon atoms or R₁ and R₂ together or R₃ and R₄ together are a divalent hydrocarbon group which forms, together with the nitrogen atom to which they are attached, a heterocycle which includes the nitrogen atom as ring member, with the proviso that at least one of the said R's is one of said hydrocarbon groups.

Thus the present invention provides a herbicidal composition containing as active ingredient a compound of formul I. The compound may be in admixture with a finely divided solid carrier or diluent, which advantageously is combined with a surface active agent so that the composition is a wettable powder. Alternatively the compound may be in a liquid carrier or solvent for the compound, combined with a surface active agent.

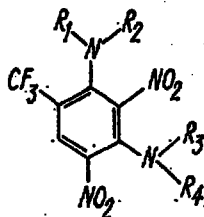
The present invention provides also a method of killing weeds which comprises applying to the locus thereof a phytotoxic amount of a compound of formula I. The compound may be applied as a pre-emergence treatment to soil in which the weeds would otherwise grow. Alternatively the compound may be applied to the foliage or leaves present in an economic crop in amount sufficient to kill the weeds but not sufficient to substantially damage the crop. These compounds, especially those in which X is $-\text{CF}_3$, are particularly valuable for the control of weeds in the presence of corn, rice, cotton or soybeans.

The novel compounds of the present invention are compounds of the formula:—

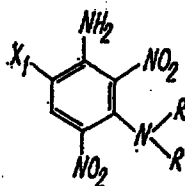


wherein X is a halogen atom or trifluoromethyl group, and each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or an aliphatic hydrocarbon group which may be substituted by a halogen atom, a hydroxy group or an alkoxy group of 1 to 4 carbon atoms or R_1 and R_2 combined or R_3 and R_4 combined form together with the nitrogen atom to which they are attached a heterocycle which includes the nitrogen atom as ring member, with the proviso that at least one of the said R's is one of said hydrocarbon group, but R_1 and R_2 are both hydrogen when X is a halogen atom.

Thus the invention provides as novel compounds, compounds of the formula:—



wherein R_1 , R_2 , R_3 and R_4 are each hydrogen, alkyl, alkenyl or alkynyl, at least one of said R's being a hydrocarbon group, or $\text{R}_1 + \text{R}_2$ and/or $\text{R}_3 + \text{R}_4$ represent an alkylene group having from 2 to 6 carbon atoms in the chain and compounds of the formula:—



in which X_1 is halogen and each R is hydrogen or alkyl of 1 to 5 carbon atoms so long as the total number of carbon atoms represented by $\text{R} + \text{R}$ is from 3 to 8.

For convenience in naming the compounds, the amino nitrogen adjacent to the halo or trifluoromethyl group X is referred to as N^1 and the amino nitrogen between the nitro groups on the ring is referred to as N^2 . Thus, the nitro substituents are in the 2 and 4 position of the aromatic ring and the $-\text{X}$ group is in the 6 position of the aromatic ring. It will be noted from the above definition that either the N^1 or N^2 amino nitrogen must have at least one substituent thereon thereby excluding the unsubstituted compound having two amino ($-\text{NH}_2$) groups. Such unsubstituted compounds, i.e. those in which each of R_1 , R_2 , R_3 and R_4 is hydrogen, are less effective as selective herbicides and are not compounds of the invention.

Typical examples of the groups represented by R_1 , R_2 , R_3 and R_4 as defined above are hydrogen and the lower alkyl, lower alkenyl, and lower alkynyl groups having up to 6 carbon atoms, including the cyclic analogues thereof as well as the halo, hydroxy, and lower alkoxy substituted derivatives thereof. Representative groups are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *n*-pentyl, *sec*-pentyl, *n*-hexyl, allyl, 2-butenyl, 2-butyryl, 3-butyryl, methallyl, 2-pentyryl, 2-hydroxyethyl, 2-bromo-

ethyl, 2-methoxyethyl, 3-ethoxypropyl, 2,2-dimethoxyethyl, 2-chloroallyl, 3-chloropropyl, 4-hydroxy-2-butyryl, 1-methyl-2-methoxyethyl, 2-bromoallyl, propynyl, 4-chloro-2-butenyl, 4-bromo-1-butenyl, 3-iodo-2-pentenyl, 4-chloro-2-butyryl, cyclohexyl, cyclopropyl, cyclobutyl and cyclohexenyl.

Furthermore, R_1-R_2 and/or R_3-R_4 can represent a fragment of a ring of which the amino nitrogen is a part thereof, such as illustrated by the structure



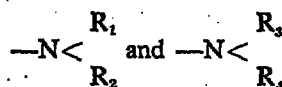
in which Z is an alkylene group having from 2 to 6 carbon atoms in the chain, and optionally other atoms such as oxygen and nitrogen. Such linkages include the dimethylene, trimethylene, tetramethylene, diethyleneoxy, diethyleneimino, and hexamethylene groups.

A preferred class of compounds according to this invention is those in which X is trifluoromethyl, R_1 is hydrogen, R_2 and R_3 are each hydrogen or alkyl of 1 to 5 carbon atoms and R_4 is alkyl of 1 to 5 carbon atoms. Thus, representative examples of alkyl are methyl, ethyl, *n*-propyl, isopropyl, *sec*-butyl and *sec*-pentyl. Preferably the total number of carbon atoms represented by $R_1+R_2+R_3+R_4$ is 4 to 8. Compounds in which both R_1 and R_2 are hydrogen represent a preferred sub-class of the trifluoromethyl compounds of this invention.

Representative examples of such preferred compounds are:

- N^1 - *sec* - butyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine
- N^1 - ethyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - methyl - N^3 - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - ethyl - N^3 - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - methyl - N^3, N^3 - di - *n* - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine
- N^3, N^3 - di - *n* - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - methyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - *n* - propyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^1 - *sec* - pentyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine
- N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^3 - (3 - pentyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^3 - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine
- N^3 - (1 - methyl - 2 - methoxyethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine

Another class of compounds preferred as active ingredients of herbicidal compositions according to this invention is those in which X is halogen, and R_1 , R_2 , R_3 and R_4 are each a hydrogen atom or an alkyl, alkenyl or alkynyl group, at least the R being an alkyl, alkenyl or alkenyl group; and particularly those in which X is bromo or chloro, R_1 is hydrogen, R_2 is selected from hydrogen and alkyl of 1 to 3 carbon atoms and R_3 and R_4 are each selected from hydrogen and alkyl of 1 to 5 carbon atoms. Preferably, the compounds are unsymmetrical; that is,

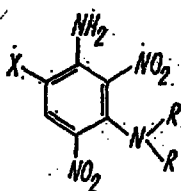


are different, and the total number of carbon atoms represented by R_3+R_4 is 2 to 8.

Representative examples of such preferred compounds are

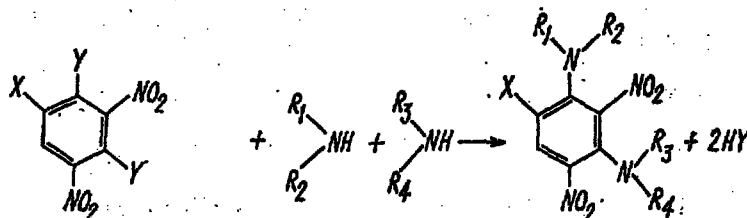
N¹-ethyl-N³,N³-diethyl-2,4-dinitro-6-bromo-1,3-phenylenediamine
 N¹-methyl-N³-*sec*-butyl-2,4-dinitro-6-chloro-1,3-phenylenediamine
 N¹-ethyl-N³-*sec*-butyl-2,4-dinitro-6-bromo-1,3-phenylenediamine
 N¹-methyl-N³,N³-di-*n*-propyl-2,4-dinitro-6-chloro-1,3-phenylenediamine
 N³,N³-di-*n*-propyl-2,4-dinitro-6-chloro-1,3-phenylenediamine
 N¹-methyl-N³,N³-diethyl-2,4-dinitro-6-chloro-1,3-phenylenediamine
 N³,N³-diethyl-2,4-dinitro-6-bromo-1,3-phenylenediamine
 N¹-*sec*-pentyl-N³,N³-dimethyl-2,4-dinitro-6-chloro-1,3-phenylenediamine.

A particularly preferred class of compounds, which are all compounds of the invention, can be illustrated by the formula:—



in which X is bromo or chloro and each R is selected from hydrogen and alkyl of 1 to 5 carbon atoms, the total number of carbon atoms represented by R+R being 3 to 8.

The compounds of this invention are either crystalline solids or high boiling liquids. Generally they are only slightly soluble in water and are moderately soluble in the usual organic solvents such as ethanol, acetone, ether and benzene. The compounds are readily prepared by reaction of two amines or one amine and ammonia with a 1-X-2,4-dihalo-3,5-dinitrobenzene according to the following equation:—



in which Y is a reactive halogen such as chlorine or bromine, R₁, R₂, R₃ and R₄ have the significance previously assigned, and X is a trifluoromethyl group or a halogen atom.

When R₁ and R₂ are the same as R₃ and R₄, that is when the substituted N¹ amino group is the same as the substituted N³ amino group in the resultant product, the reaction takes place in one step using at least two moles of amine for each mole of 2,4-dihalo-3,5-dinitrobenzene. The hydrogen halide can be neutralised by excess amine or a tertiary amine. When R₁ and R₂ are different from R₃ and R₄, the reaction requires two steps in which a different amine (or ammonia) is employed in each step. In the first step two moles of the amine forming the N³ group is reacted with one mole of the 1-X, 2,4-dihalo-3,5-dinitrobenzene. The first halogen atom replaced is that between the nitro groups on the aromatic ring. This step is advantageously carried out in a non-polar solvent such as a hydrocarbon in which the amine hydrohalide is insoluble so that it can be removed by filtration. In the second step two moles of the amine forming the N¹ group is reacted with one mole of the monoamino-substituted compound to form the unsymmetrically substituted 1,3-phenylenediamine compound. The second reaction can take place in a sealed reaction vessel, such as a sealed tube or an autoclave, to avoid losses of amine and provide easy control of the reaction, or at atmospheric pressure in the presence of a solvent, such as an alcohol, in which the amine is highly soluble. In the case of higher boiling amines it is not necessary to use a sealed reaction vessel for the reaction but it is sufficient merely to carry it out in the presence of a suitable solvent.

A reaction temperature in the range of from about 20° to about 120° C., or up to about 100° C. when X is —CF₃, is preferably employed to give good yields of the desired product and a satisfactory rate of reaction, both in the case of using a sealed reaction vessel and when the reactants are brought together at atmospheric pressure. Hydrogen halide is formed as a by-product and, in the presence of excess amine, is converted to the amine hydrohalide which can be readily removed by washing with water or by filtration after dissolution of the product in a suitable solvent. The desired products can be purified by well known procedures such as by recrystallisation.

The 2,4-dihalo-3,5-dinitrobenzotrifluoride starting materials are readily prepared by nitration of the 2,4-dihalobenzotrifluoride with a mixture of fuming nitric and fuming sulphuric acids at a temperature below about 80° C.

The following Examples I—VIII describe preparation of representative compounds of this invention, while Example IX describes the preparation of a compound which may be active ingredient in a composition of the invention.

EXAMPLE I

N¹,N³-bis(Diethyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

A heavy walled glass reaction tube of about 50 ml. capacity was charged with 5 grams (0.0163 mole) of 2,4-dichloro-3,5-dinitrobenzotrifluoride, 30 ml. of ethanol and 20 ml. of diethylamine. The reaction tube was sealed and heated in a bath at 94°—99° C. for 46.5 hours. The cooled reaction tube was then opened and the contents evaporated to dryness to give a solid residue. The residue was extracted with 200 ml. of refluxing diethyl ether and the insoluble amine hydrochloride was separated therefrom by filtration. The ether extract was evaporated to dryness and the residue dissolved in 40 ml. of refluxing 95% ethanol and 10 ml. of water. Upon cooling, the product crystallised and was isolated by filtration, obtaining the desired product (30% yield) as a crystalline solid, melting at 72.5°—74.5° C. After recrystallisation, the product melts at 74°—75° C.

Analysis: Calculated: C, 47.61; H, 5.60; N, 14.81
Found: C, 47.34; H, 5.58; N, 14.64.

EXAMPLE II

N¹,N³-bis(Dimethyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

This compound was prepared in a similar manner by reaction of 2,4-dichloro-3,5-dinitrobenzotrifluoride with dimethylamine. The crystalline product melts at 125.5°—126.5° C.

Analysis: Calculated: C, 41.00; H, 4.07; N, 17.39
Found: C, 40.91; H, 4.01; N, 17.54.

EXAMPLE III

N¹,N³-bis(Di-*n*-propyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

This compound was prepared in a similar manner by reaction of 2,4-dichloro-3,5-dinitrobenzotrifluoride with di-*n*-propylamine. The product is a high boiling oil.

EXAMPLE IV

(a) N,N-di-*n*-propyl-3-chloro-2,6-dinitro-4-trifluoromethylaniline

A heavy walled glass reaction tube of approximately 50 ml. capacity was charged with 7.0 grams (0.023 mole) of 2,4-dichloro-3,5-dinitrobenzotrifluoride, 4.64 grams (0.0458 mole) of di-*n*-propylamine and 40 ml. of absolute ethanol. The tube was sealed and heated in an oil bath at 94°—99° C. for 98 hours. The cooled reaction mixture was then evaporated to dryness to give an oily residue which was extracted with boiling diethyl ether. The insoluble di-*n*-propylamine hydrochloride was removed by filtration and washed with additional ether. The combined ether filtrates were evaporated to give an oily orange residue which was dissolved in 100 ml. of absolute ethanol and decolourised with activated charcoal. The ethanol and volatiles were removed by evaporation under reduced pressure to give the product (6.77 grams) as a viscous reddish oil.

(b) N²,N³-di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

A glass reaction tube was charged with 4.0 grams (0.0108 mole) of N,N-di-*n*-propyl-3-chloro-2,6-dinitro-4-trifluoromethylaniline, 5.82 grams (0.0237 mole) of 6.95% ethanolic ammonia and 35 ml. of ethanol. The tube was sealed and heated in an oven

at 100° C. for 68 hours. The contents of the tube were cooled and the ethanol removed by evaporation. Water was added to the solid orange residue to dissolve the ammonium chloride and the insoluble product was separated by filtration. The product was dissolved in refluxing 95% ethanol. Upon cooling, orange needles and a yellow powder crystallised. The yellow powder was identified as 2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine and was separated from the desired product by filtration after extraction with boiling hexane. The desired product dissolved in the hexane and was isolated from the filtrate by evaporation of the hexane. The residue was recrystallised from 95% ethanol to give orange needles, m.p. 124°—125° C.

Analysis: Calculated: N=15.99
 Found: N=16.00.

EXAMPLE V

(a) N-(3-pentyl)-3,4-dichloro-2,6-dinitroaniline

3-Pentylamine (6.00 g.; 0.0688 mole) was added to a stirred solution of 1,2,4-trichloro-3,5-dinitrobenzene (9.338 g.; 0.0344 mole) in 200 ml. of cyclohexane over a 15 minute period. After stirring at room temperature for 1 hour, the reaction mixture was heated at reflux temperature for 17 hours and then evaporated to dryness under reduced pressure. The residue was extracted with 250 ml. of boiling cyclohexane which was decanted and stripped. This residue was then taken up in chloroform, extracted with 3N hydrochloric acid, then water, dried over sodium sulphate, filtered, and the chloroform removed by distillation. The residual oil was taken up in 25 ml. of *n*-hexane, cooled and filtered to give 0.5 g. of unreacted starting material. The filtrate was stripped leaving 9.24 g. (83.3%) of N-(3-pentyl)-3,4-dichloro-2,6-dinitroaniline as an oil which was identified by its nuclear magnetic resonance spectrum.

(b) N³-(3-pentyl)-6-chloro-2,4-dinitro-1,3-phenylenediamine

A mixture of 5.00 g. (0.0155 mole) of N-(3-pentyl)-3,4-dichloro-2,6-dinitroaniline and 6.89 g. (0.0310 mole) of a 7.66% solution of ammonia in absolute ethanol was sealed in a tube with about 30 ml. of absolute ethanol. After heating for 72 hours at 94° C., the reaction mixture was stripped and the residue triturated with 500 ml. of water. Filtration and crystallisation of the solid from ethanol gave 1.89 g. (40.3%) of crude product, m.p. 118.5—121.5° C. This was taken up in 60 ml. of hot cyclohexane, filtered, stripped, and the residue recrystallised from 95% ethanol to give the desired product as shiny, orange rectangles, m.p. 119.3°—120.6° C.

EXAMPLE VI

N³,N³-diethyl-6-chloro-2,4-dinitro-1,3-phenylenediamine

This compound was prepared in a similar manner to Example V by reaction of N,N-diethyl-3,4-dichloro-2,6-dinitroaniline with ammonia. The crystalline product melts at 110°—111° C.

EXAMPLE VII

N³,N³-di-*n*-propyl-6-bromo-2,4-dinitro-1,3-phenylenediamine

This compound was prepared in a similar manner to Example V by reaction of N,N-di-*n*-propyl-3,4-dibromo-2,6-dinitroaniline with ammonia. The crystalline product melts at 119°—120° C.

EXAMPLE VIII

(a) N,N-di-*n*-propyl-3-chloro-2,6-dinitro-4-fluoroaniline

A mixture of 8.0 g. (0.0314 mole) of 2,4-dichloro-3,5-dinitrofluorobenzene, 6.35 g. (0.0628 mole) of di-*n*-propylamine, and 75 ml. of cyclohexane was heated at 58°—72° C. for 15.5 hours. The di-*n*-propylamine hydrochloride was removed by filtration and the solvent evaporated from the filtrate leaving an oil. The oil was taken up in cold pentane, filtered, and evaporated at reduced pressure leaving 10.03 g. (96.5%) of N,N-di-*n*-propyl-3-chloro-2,6-dinitro-4-fluoroaniline, identified by its nuclear magnetic resonance spectrum.

(b) N³,N³-di-*n*-propyl-2,4-dinitro-6-fluoro-1,3-phenylenediamine

A solution of 7.34 g. (0.0224 mole) of N,N-di-*n*-propyl-3-chloro-2,6-dinitro-4-fluoroaniline, 12.87 g. (0.0458 mole) of a 6.06% solution of ammonia in absolute ethanol, and 2.317 g. (0.0229 mole) of triethylamine in about 35 ml. of absolute ethanol was heated in a sealed Pyrex tube for 72 hours at 98° C. ["Pyrex" is a registered Trade Mark]. The contents were distilled to dryness at reduced pressure and extracted twice with 100 ml. portions of boiling cyclohexane. The combined filtered cyclohexane extracts were evaporated to dryness and the residual oil taken up in hot *n*-hexane, filtered, and evaporated to an oil. This crude oil was chromato-

graphed over 250 g. of activated alumina using pentane, 2:1 pentane-benzene and 1:2 pentane-benzene, respectively, as eluting solvents. After an initial fraction of N^1, N^1, N^3, N^3 - tetra - *n* - propyl - 2,4 - dinitro - 6 - fluoro - 1,3 - phenylenediamine was collected, N^3, N^3 - di-*n*-propyl-2,4-dinitro-6-fluoro-1,3-phenylenediamine was obtained. Recrystallisation twice from aqueous ethanol gave the product as orange needles, m.p. 90.5°—91.5° C.

EXAMPLE IX

N^1, N^3 - diethyl-6-chloro-2,4-dinitro-1,3-phenylenediamine

To a stirred solution of 20 ml. of 70% aqueous ethylamine in 50 ml. of ethanol was added, dropwise at room temperature, a solution of 6.79 g. (0.025 mole) of 1,2,4-trichloro-3,5-dinitrobenzene dissolved in 200 ml. of ethanol. an additional 20 ml. of 70% aqueous ethylamine was then added to the stirred mixture. The resultant solution was refluxed for one hour and then stirred at room temperature overnight. The mixture was cooled in an ice water bath and then filtered to obtain 5.70 g. of the desired product as an orange solid, m.p. 96.5°—98.0° C. After recrystallisation from ethanol, the compound melts at 97.5°—98.5° C.

Other compounds effective as the active ingredient in compositions according to the invention in which X is halo are:

- N^3 - *sec*-butyl-2,4-dinitro-6-chloro-1,3-phenylenediamine; m.p. 124.5°—125.5° C.
- N^3 - *sec*-butyl-2,4-dinitro-6-bromo-1,3-phenylenediamine; m.p. 140.5°—141.5° C.
- N^3, N^3 - diethyl-2,4-dinitro-6-bromo-1,3-phenylenediamine; m.p. 107°—109° C.
- N^3 - isopropyl-2,4-dinitro-6-bromo-1,3-phenylenediamine; m.p. 148°—150° C.
- N^3 - *sec*-amyl-2,4-dinitro-6-bromo-1,3-phenylenediamine; m.p. 115°—116.5° C.
- N^3 - (1 - methyl - 2 - methoxyethyl) - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 138.5°—141° C.
- N^1, N^3 - bis(2 - chloroallyl) - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 99.5°—100.5° C.
- N^1, N^3 - dicyclopropyl-2,4-dinitro-6-chloro-1,3-phenylenediamine; m.p. 112°—113° C.
- N^1, N^3 - diallyl-2,4-dinitro-6-bromo-1,3-phenylenediamine; m.p. 82.5°—83.5° C.
- N^1, N^1 - dimethyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 67°—68° C.
- N^1 - ethyl - N^3 - *sec*-butyl-2,4-dinitro-6-chloro-1,3-phenylenediamine; m.p. 72.5°—74° C.
- N^3, N^3 - pentamethylene - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 123.5°—124.5° C.
- N^1, N^1, N^3, N^3 - tetra-*n*-propyl-2,4-dinitro-6-fluoro-1,3-phenylenediamine; oil
- N^1 - methyl - N^3 - *sec*-butyl-2,4-dinitro-6-chloro-1,3-phenylenediamine; m.p. 105°—108° C.
- N^3, N^3 - di - *n* - propyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 122.5°—123.5° C.
- N^1, N^1 - dimethyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 77°—78° C.
- N^3, N^3 - diethyl - 2,4 - dinitro - 6 - fluoro - 1,3 - phenylenediamine; m.p. 146°—147.5° C.
- N^1 - methyl - N^3, N^3 - di - *n* - propyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; oil
- N^1 - methyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine; m.p. 82.5°—83.5° C.
- N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - bromo - 1,3 - phenylenediamine; m.p. 143°—143.5° C.
- N^1, N^3 - dicyclohexyl - 2,4 - dinitro - 6 - bromo - 1,3 - phenylenediamine; m.p. 113°—114° C.

Other compounds according to the invention in which X is trifluoromethyl are:

- N^1 - ethyl - N^3 - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 92.5°—94° C.
- N^1 - *sec* - butyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; oil
- N^1 - *sec* - butyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; oil
- N^1 - methyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 71.5°—73.5° C.

	N^1 - methyl - N^3, N^3 - di - <i>n</i> - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 48.5°—50.5° C.		
	N^1, N^1 - di - <i>n</i> - propyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 39.5°—40.5° C.		
5	N^1 - ethyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; 54—55.5° C.	5	5
	N^1, N^1 - diethyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 45°—46° C.		
10	N^1 - methyl - N^3 - <i>sec</i> - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 81°—83° C.	10	10
	N^1, N^1 - dimethylene - N^3 - <i>sec</i> - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 92°—93° C.		
	N^1 - propargyl - N^3, N^3 - di - <i>n</i> - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; oil		
15	N^1 - propargyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; oil	15	15
	N^1, N^1 - diethyl - N^3 - ethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 64.5°—65.5° C.		
20	N^1 - propargyl - N^3 - <i>sec</i> - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 53°—54° C.	20	20
	N^1, N^1 - dimethyl - N^3, N^3 - di - <i>n</i> - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 58.5°—59.5° C.		
	N^1, N^1 - dimethyl - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 114°—116° C.		
25	N^1, N^1 - diethyl - N^3 - <i>sec</i> - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; oil	25	25
	N^1 - ethyl - N^3, N^3 - di - <i>n</i> - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; oil		
30	N^1, N^1 - dimethylene - N^3, N^3 - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; oil	30	30
	N^1 - propargyl - N^3, N^3 - dimethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 66°—67° C.		
	N^1 - (2 - hydroxyethyl) - N^3 - <i>sec</i> - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 57.5°—58.5° C.		
35	N^3 - cyclopentyl - N^3 - methyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 87°—88.5° C.	35	35
	N^3 - (1 - methyl - 2 - methoxyethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 120.5°—121.5° C.		
40	N^3 - (2,2 - dimethoxyethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 137°—139° C.	40	40
	N^3 - (3 - chloropropyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 94°—94.5° C.		
	N^3 - (2 - bromoethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 149°—150° C.		
45	N^3, N^3 - bis(2 - methoxyethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 93°—94° C.	45	45
	N^3 - cyclopropyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 180°—181.5° C.		
50	N^1 - methyl - N^3 - (3 - pentyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 73.5°—74.5° C.	50	50
	N^3 - <i>sec</i> - amyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 105.5°—106.5° C.		
	N^1 - methyl - N^3, N^3 - diethyleneoxy - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 201°—203° C.		
55	N^3 - methyl - N^3 - ethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 89°—89.5° C.	55	55
	N^3, N^3 - diallyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 72°—73° C.		
60	N^1 - methyl - N^3, N^3 - pentamethylene - 2,4 - dinitro - 6 - trifluoromethyl - 1,3-phenylenediamine; m.p. 112.5°—113.5° C.	60	60
	N^3 - (pent - 3 - yl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 119.5°—120.5° C.		
	N^1 - methyl - N^3 - cyclohexyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 127.5°—128.5° C.		

N³ - (2 - chloroallyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 102°—103° C.

N³ - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 126.5°—127.5° C.

N³,N³ - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 98°—99° C.

N³,N¹ - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 85°—86° C.

N³,N¹ - di - *n* - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 75.5°—76.5° C.

N³ - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 58°—60° C.

To complete this account of preparation of compounds of the invention, we describe next by way of example the preparation of an intermediate.

2,4-dichloro-3,5-dinitrobenzotrifluoride

Fuming sulphuric acid (600 ml.) containing 30—33% free SO₃ was stirred in a two-litre, three-necked flask immersed in an ice bath. Fuming 90% nitric acid (585 ml.) was added followed by 148.8 grams (0.692 mole) of 2,4-dichlorobenzotrifluoride. This stirred slurry then was heated to 76° C. and held at 76±1° C. for 96 hours. The mixture was cooled and the acid was drained from the crust of crystalline product. Water (1000 ml.) was added to the broken up solid and the stirred slurry extracted with 500 ml. of toluene. The toluene solution with another 500 ml. of toluene added was washed successively with water (500 ml.), twice with 500 ml. of 5% sodium bicarbonate solution, and finally with water (500 ml.). Removal of the toluene by evaporation at reduced pressure and drying overnight gave 166.6 grams (79%) of the desired 2,4-dichloro-3,5-dinitrobenzotrifluoride, m.p. 67°—72° C. After recrystallisation from ethanol the material melts at 74°—75° C.

The compounds of this invention are excellent herbicides and are especially useful as selective herbicides for controlling weeds in the presence of desirable crops, especially the grassy weeds such as, for example, foxtail, water grass, and crabgrass. Many of the compounds of this invention, especially those in which X is —CF₃, may be used in controlling weeds in desirable grassy crops such as corn and rice, as well as the small grains, and also the broad leaf crops such as cotton and soy beans. Also, many of the preferred compounds are effective in controlling wild oats which constitute a major problem in small grain crops such as wheat and barley.

The compounds which are found most effective as herbicides according to the present invention are:

N³,N³ - di - *n* - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; 124°—125° C.

N³,N³ - diethyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 98°—99° C.

N³ - *sec* - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 126.5°—127.5° C.

N³ - ethyl - N³ - propyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine

N³ - (pent - 3 - yl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 119.5°—120.5° C.

N³ - (1 - methyl - 2 - methoxyethyl) - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine

N³,N³ - diallyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine; m.p. 72°—73° C.

N³ - ethyl - N³ - butyl - 2,4 - dinitro - 6 - trifluoromethyl - 1,3 - phenylenediamine

N³,N³ - diethyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine

N³,N³ - di - *n* - propyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine.

Water grass and related weeds are a serious problem in rice and the discovery of an effective selective herbicide for this problem is a significant advancement in the art. Such a discovery is surprising and unexpected in view of the phytotoxicity of many other aromatic amine derivatives to grassy crops such as rice. It has also been found that the specific phenylenediamines of this invention are much less volatile than many other substituted aromatic amines and will move better in the soil, as well as possessing better ultra-violet stability.

The compounds can be applied as both a pre-emergence or a post-emergence treatment; that is they can be applied to soil in which the weeds will grow or they can be used to kill or suppress the growth of weeds or to kill or prevent the emergence of seedlings of undesirable plants. Thus, the compounds can be used to control the growth of weeds by applying a phytotoxic amount of one or more of the active compounds of this invention to the locus to be protected, that is, soil in which the weeds are growing or will grow or the foliage of the growing plants. "Weeds" as used herein is meant to include any plant growth which is undesirable.

Generally an application rate of from about 0.1 to about 25 pounds of one or more of the active compounds per acre is effective in controlling plant growth. Preferably an application rate of from about 0.25 to about 5 pounds per acre is employed. At such rates the undesirable weeds are killed or stunted with little or no injury to desirable crops.

The following Examples illustrate the herbicidal activity of typical compounds of this invention.

EXAMPLE X

The compounds to be tested were evaluated as preemergence herbicides on a broad class of representative weeds and crops. Green-house flats were planted to pigweed, cheat, wild oats, foxtail, morning glory, water grass, rice, sugar beets, cotton, corn, barley, and soybeans. On the same day of planting the flats were sprayed with an ethanol solution of the compound to be tested at a rate of two pounds per acre. The flats were kept in the green-house and watered when needed. Twenty-one days after treatment, the plants were evaluated for herbicidal activity and rated on a 0 to 9 scale in which 0=no effect; 5=substantial injury with slight kill and 9=complete kill.

The following results were obtained.

TABLE I

Compound	Activity*											
DTP = 2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine)	P	CH	WO	F	M	W	R	SB	CO	CR	B	SO
N ¹ -ethyl-N ³ -sec-butyl-DTP	9	0	5	9	0	9	0	4	3	1	0	0
N ¹ -methyl-N ³ -sec-butyl-DTP	9	1	8	9	1	9	0	4	1	4	0	1
N ¹ ,N ¹ -dimethyl-N ³ ,N ³ -diethyl-DTP	9	1	2	7	0	9	0	3	0	0	0	0
N ¹ -sec-butyl-N ³ ,N ³ -dimethyl-DTP	9	3	8	9	1	9	0	1	0	1	1	1
N ¹ -sec-butyl-N ³ ,N ³ -diethyl-DTP	2	0	3	9	0	7	0	0	0	0	1	0
N ¹ ,N ¹ -dimethylene-N ³ ,N ³ -di-n-propyl-DTP	8	1	5	6	0	4	0	1	1	0	0	0

*P = pigweed

M = morning glory

CO = cotton

CH = cheat

W = water grass

CR = corn

WO = wild oats

R = rice

B = barley

F = foxtail

SB = sugar beets

SO = soybeans

EXAMPLE XI

The compounds to be tested were evaluated as both a pre-emergence and post-emergence treatment on a broad class of weeds and crops. Green-house flats were planted to the species tested in Example X and the flats sprayed on the same day as planting with an ethanol solution of the compound to be tested at a rate of 2 pounds per acre.

Another set of flats with the same plants was treated after the plants had emerged and were about one inch in height. These flats were also sprayed with an ethanol solution of the compound at a rate of 2 pounds per acre in order to determine post-emergence activity. The flats were kept in the green-house and watered when needed. Twenty-two days after treatment the flats were evaluated and rated as described in Example X. The following results were obtained.

TABLE II

Plant Specie	Compound A		Compound B		Compound C	
	Pre	Post	Pre	Post	Pre	Post
Pigweed	8	4	9	4	8	3
Cheat	2	2	3	0	3	2
Wild Oats	9	3	9	3	9	3
Foxtail	9	8	9	8	9	5
Morning Glory	0	3	4	4	0	3
Water grass	9	8	9	9	9	7
Rice	0	0	0	0	0	0
Sugar beets	6	1	9	4	2	1
Cotton	0	6	4	4	0	3
Corn	0	0	4	2	0	0
Barley	0	0	1	0	0	1
Soybeans	0	3	3	4	0	3

Compound A = N¹-methyl-N³,N³-di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

Compound B = N³,N³-di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

Compound C = N¹-methyl-N³,N³-diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine

EXAMPLE XII

N³-(1-methyl-2-methoxyethyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine is especially useful for controlling weeds in corn and cotton. For example, an ethanol solution of the compound was applied to soil at a rate of 0.25 pound per acre and then incorporated by mixing in a green-house flat. On the same day, foxtail, wild oats, millet, water grass, crabgrass, pigweed, velvet leaf and corn were planted in the mixed treated soil. The flats were kept in the green-house and watered when needed. Fourteen days after treatment the flats were examined and the plants rated for herbicidal activity, as described in Example X. The following results were obtained.

TABLE III

	Plant Specie	Activity Rating	
	Foxtail	8	
	Wild oats	8	
5	Millet	9	5
	Water grass	9	
	Crabgrass	9	
	Pigweed	9	
	Velvet leaf	5	
10	Corn	0	10
	Cotton	0	

EXAMPLE XIII

Green-house flats were planted to soybeans, velvet leaf, oats and millet. On the same day as planting the flats were sprayed with an ethanol solution of the compound to be tested at a rate of 5 pounds per acre. The flats were kept in the green-house and watered when needed. Twenty-one days after treatment the flats were examined and the plants rated for herbicidal activity and rated on a 0 to 9 scale in which 0=no effect; 5=substantial injury with slight kill, and 9=complete kill. The following results were obtained.

TABLE IV

Compound	Activity*			
(DPD = 2,4-dinitro-1,3-phenylenediamine)	SO	VL	O	MI
N ³ ,N ³ -diethyl-6-bromo-DPD	3	8	3	9
N ³ ,N ³ -di- <i>n</i> -propyl-6-chloro-DPD	1	4	2	9
N ¹ -methyl-N ³ ,N ³ -diethyl-6-chloro-DPD	0	0	2	9
N ¹ -ethyl-N ³ ,N ³ -diethyl-6-chloro-DPD	0	0	1	9
N ³ ,N ³ -di- <i>n</i> -propyl-6-bromo-DPD	2	5	3	9
N ³ - <i>sec</i> -butyl-6-chloro-DPD	2	3	1	9
N ¹ ,N ³ -diethyl-6-bromo-DPD	0	0	0	4
N ³ ,N ³ -diethyl-6-chloro-DPD	0	3	3	9
N ¹ ,N ³ -diethyl-6-chloro-DPD	2	0	2	6
N ³ -(3-pentyl)-6-chloro-DPD	2	5	6	9
N ³ ,N ³ -pentamethylene-6-chloro-DPD	0	0	2	7
N ³ -(1-methyl-2-methoxyethyl)-6-chloro-DPD	2	4	2	9
N ³ ,N ³ -di- <i>n</i> -propyl-6-fluoro-DPD	2	5	8	9
N ³ - <i>sec</i> -amyl-6-bromo-DPD	0	3	2	9
N ³ ,N ³ -dimethyl-6-bromo-DPD	0	0	0	8
N ³ -ethyl-6-bromo-DPD	0	0	0	9
N ³ -isopropyl-6-bromo-DPD	1	4	0	9
N ¹ -methyl-N ³ - <i>sec</i> -butyl-6-chloro-DPD	3	5	3	9

*SO = soybeans
VL = velvet leaf

O = oats
MI = millet

EXAMPLE XIV

N^1, N^1, N^2, N^2 - tetramethyl - 2,4 - dinitro - 6 - chloro - 1,3 - phenylenediamine was applied as both a pre-emergence and post-emergence treatment to corn, millet, rye grass, oats, peas, mustard, cucumbers and snap beans. The compound was applied in an acetone-methanol solution at a rate of 25 pounds per acre. The plants were kept in a green-house and watered when needed. Thirty days after treatment, the plants were examined and the herbicidal activity rated on a 0 to 10 scale in which 0=no effect and 10=complete kill. The following results were obtained.

TABLE V

Plant	Activity Rating	
	Pre	Post
Millet	4	0
Rye Grass	9	3
Oats	7	3
Peas	0	0
Mustard	9	9
Cucumber	5	6
Snap beans	0	3
Corn	2	0

EXAMPLE XV

The compounds to be tested were evaluated as pre-emergence herbicides on a broad class of representative weeds and crops. Green-house flats were sprayed with an ethanol solution of the compound at a rate of 0.5 pounds per acre and the chemical was mixed into the top one inch layer of the soil. The flats were then planted to foxtail, wild oats, millet, watergrass, crabgrass, bush beans, morning glory, tomatoes, corn, rice, soy beans, cotton, barley, flax, and pigweed. The flats were kept in the green-house and watered when needed. Twenty-one days after planting the plants were evaluated for herbicidal activity and rated on a 0 to 9 scale in which 0=no effect; 5=substantial injury with slight kill, and 9=complete kill. The following results were obtained.

TABLE VI

Compound	Activity*														
(DPD=2,4-dinitro-1,3-phenylene-diamine)	F	WO	MI	W	CB	BB	M	T	C	R	CO	B	FX	P	SO
N ³ -sec-butyl-6-chloro-DPD	2	2	7	6	8	0	2	1	0	1	1	0	0	7	1
N ³ -sec-butyl-6-bromo-DPD	3	5	7	8	9	0	3	2	0	1	1	0	0	6	2
N ¹ -methyl-N ³ ,N ³ -diethyl-6-chloro-DPD	5	5	2	6	8	0	2	0	0	0	0	0	0	4	0
N ¹ ,N ¹ -di-methyl-N ³ ,N ³ -diethyl-6-chloro-DPD	2	5	2	7	9	1	3	2	0	0	0	0	0	6	0
*F = foxtail	BB = bush beans					CO = cotton									
WO = wild oats	M = morning glory					B = barley									
MI = millet	T = tomatoes					FX = flax									
W = watergrass	C = corn					P = pigweed									
CB = crabgrass	R = rice					SO = soybeans									

Since a relatively small amount of one or more of the active 2,4-dinitro-1,3-phenylenediamines should be uniformly distributed over the area to be treated, the compounds preferably are formulated with conventional herbicide carriers, either liquid or solid. Thus, the compounds can be impregnated on or admixed with a pulverulent solid carrier such as lime, talc, clays, Bentonite, calcium chloride, vermiculite or calcium carbonate. Alternatively, the compounds can be dissolved or suspended in a liquid carrier such as water, kerosene, alcohols, diesel oil, xylene, benzene, glycols or ketones. A surfactant preferably is included to aid in dispersion, emulsification and coverage. The surfactant can be ionic or non-ionic, and may be liquid or a solid. The use of the term "surfactant" herein is intended to include such compounds commonly referred to as wetting agents, dispersing agents and emulsifying agents. Typical surfactants include the alkylarylsulphonates, the fatty alcohol sulphates, sodium salt or naphthalenesulphonic acid, alkylaryl polyether alcohols, long chain quaternary ammonium compounds, sodium salts of petroleum-derived alkylsulphonic acids or polyoxyethylene-sorbitan monolaurate. These dispersing and wetting agents are sold under numerous trademarks and may either be pure compounds, mixtures of compounds of the same general group, or they may be mixtures of compounds of different classes. Surfactants can also be included in compositions containing a solid inert carrier.

Concentrated compositions containing the active agent which can be subsequently diluted, as with water, to the desired concentration for application to plants and soil are also provided. The advantages of such concentrates are that they are prepared by the manufacture in a form such that the user need only mix them with a locally available carrier, preferably water, thereby keeping shipping costs to a minimum while providing a product which can be used with a minimum of equipment and effort. Such concentrates may contain from about 5 to about 99 percent by weight of one or more of the active 2,4-dinitro-1,3-phenylenediamines with a carrier or diluent, which may be a liquid or a solid. Liquid carriers which are miscible with the active agent or other liquids in which the compounds may be suspended or dispersed can be used. A surfactant is also generally included to facilitate such dilution or dispersion in water. However, the surfactant itself may comprise the carrier in such concentrates.

The herbicidal compositions can include other beneficial adjuvants, such as humectants, oils and contact agents. Also, other herbicides such as the sodium borates, sodium chlorate, chlorophenoxyacetic acids, substituted uracils and ureas, triazines, benzimidazoles, carbamates, amides, and haloalkanoic acids, can be included in the formulation.

The following Examples XVI to XXI are presented to illustrate the preparation of suitable herbicidal compositions of this invention.

EXAMPLE XVI

5% N^3,N^3 -di-*n*-propyl-2,4-dinitro-6-chloro-1,3-phenylenediamine (powdered)
95% Granular clay

A granular formulation can be prepared by dry blending the above constituents until uniformly mixed in a rotary mixer. A fine spray of water is sprayed onto the mixture, while tumbling, to adhere the compound to the clay. The material is then air dried while tumbling to give a granular formulation which can be applied to the soil or vegetation by hand or by a mechanical spreader.

EXAMPLE XVII

85% N^3,N^3 -diethyl-2,4-dinitro-6-bromo-1,3-phenylenediamine
14% Bentonite clay
1% Sodium lauryl sulphate surfactant

A wettable powder formulation can be prepared by micronizing the 2,4-dinitro-1,3-phenylenediamine and mixing uniformly with powdered Bentonite clay and powdered sodium lauryl sulphate. The wettable powder can be added to water or hydrocarbon oil and mechanically agitated to ensure a uniform dispersion which can be sprayed with conventional equipment onto soil or vegetation.

EXAMPLE XVIII

25% N^1 -ethyl- N^3,N^3 -diethyl-2,4-dinitro-6-bromo-1,3-phenylenediamine
5% Aromatic sulphonate-oxide condensate surfactant
70% Xylene

The 2,4-dinitro-1,3-phenylenediamine is dissolved in xylene to form a concentrated solution. The emulsifying agent is then dissolved and a liquid formulation of an emulsifiable concentrate is obtained. The emulsifiable concentrate can be added to water to dilute it to a desired concentration, and then sprayed with conventional equipment onto soil or vegetation.

EXAMPLE XIX

5% N^1 -propargyl- N^3,N^3 -dimethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine (powdered)
95% Granular clay

A granular formulation can be prepared by dry blending the above constituents until uniformly mixed in a rotary mixer. A fine spray of water is sprayed onto the mixture, while tumbling, to adhere the compound to the clay. The material is then air dried while tumbling to give a granular formulation which can be applied to the soil or vegetation by hand or by a mechanical spreader.

EXAMPLE XX

85% N^3,N^3 -di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine
14% Bentonite clay
1% Sodium lauryl sulphate surfactant

A wettable powder formulation can be prepared by micronizing the 2,4-dinitro-1,3-phenylenediamine and mixing uniformly with powdered Bentonite clay and powdered sodium lauryl sulphate. The wettable powder can be added to water on hydrocarbon oil and mechanically agitated to ensure a uniform dispersion which can be sprayed with conventional equipment onto soil or vegetation.

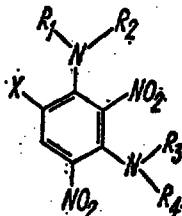
EXAMPLE XXI

25% N^1 -ethyl- N^3,N^3 -diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine
5% Aromatic sulphonate-oxide condensate surfactant
70% Xylene

The 2,4-dinitro-1,3-phenylenediamine is dissolved in xylene to form a concentrated solution. The emulsifying agent is dissolved and a liquid formulation of an emulsifiable concentrate is obtained. The emulsifiable concentrate can be added to water to dilute it to a desired concentration, and then sprayed with conventional equipment onto soil or vegetation.

WHAT WE CLAIM IS:—

1. A herbicidal composition containing as active ingredient a compound of the formula



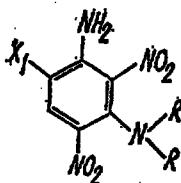
5 wherein X is a halogen atom or trifluoromethyl group and each of R₁, R₂, R₃ and R₄ is independently a hydrogen atom or aliphatic hydrocarbon group which may be substituted by a halogen atom, a hydroxy group or an alkoxy group of 1—4 carbon atoms, or R₁ and R₂ together or R₃ and R₄ together are a divalent hydrocarbon group forming the complement to a heterocycle which includes the nitrogen atom as a ring member, with the proviso that at least one of said R's is a said hydrocarbon group, with an inert, solid carrier or with an inert, liquid solvent or diluent and a surface active agent.

10 2. A herbicidal composition according to claim 1 characterised in that X is halogen and R₁, R₂, R₃ and R₄ are each a hydrogen atom or an alkyl, alkenyl or alkynyl group, at least one R being an alkyl, alkenyl or alkynyl group.

15 3. A herbicidal composition according to claim 2, characterised in that X is bromo or chloro, R₁ is hydrogen, R₂ is selected from hydrogen and alkyl of 1 to 3 carbon atoms and R₃ and R₄ are each selected from hydrogen and alkyl of 1 to 5 carbon atoms.

20 4. A herbicidal composition according to claim 2 in which $\text{—N} \begin{smallmatrix} \text{R}_1 \\ \text{R}_2 \end{smallmatrix}$ is different from $\text{—N} \begin{smallmatrix} \text{R}_3 \\ \text{R}_4 \end{smallmatrix}$ and R₃ and R₄ contain in total from 2 to 8 carbon atoms.

5. A herbicidal composition according to claim 4, characterised in that the active ingredient is a compound of formula:



25 in which X is bromo or chloro and each R is selected from hydrogen and alkyl of 1 to 5 carbon atoms, the total number of carbon atoms represented by R+R being 3 to 8.

6. A herbicidal composition according to claim 4 or 5 in which X is Chloro.

30 7. A herbicidal composition according to claim 1, characterised in that X is —CF₃, R₁ is hydrogen, R₂ and R₃ are each hydrogen or alkyl of 1 to 5 carbon atoms and R₄ is alkyl of 1 to 5 carbon atoms.

8. A herbicidal composition according to claim 7, characterised in that R₁ and R₂ are hydrogen, R₃ is hydrogen or alkyl of 1 to 5 carbon atoms and R₄ is alkyl of 1—5 carbon atoms.

35 9. A herbicidal composition according to claim 7 or 8, in which R₁, R₂, R₃ and R₄ contain in total from 4 to 8 carbon atoms.

10. A herbicidal composition according to claim 1, characterised in that the active ingredient is one of the ten substituted phenylene-diamines hereinbefore identified as having marked herbicidal activities.

40 11. A herbicidal composition according to the preceding claims, characterised in that it comprises the active ingredient together with a solvent or liquid diluent therefor and a surface-active agent.

12. A herbicidal composition according to any of claims 1 to 10, characterised in that it comprises the active ingredient together with a finely divided solid carrier.





* C L M S *

1,268,584

17

13. A herbicidal composition according to claim 12 characterised in that it comprises also a surface-active agent.

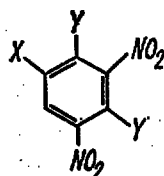
14. A method of controlling weed growth which comprises applying to the locus of the weeds a phytotoxic amount of a herbicidal compound as defined in any of claims 1-10.

15. A method according to claim 14 in which the herbicidal compound is applied as a pre-emergence treatment to soil in which the weeds would otherwise grow.

16. A method as claimed in claim 14 in which the herbicidal compound is applied to the foliage of weeds growing in the presence of an economic crop in quantity sufficient to kill the weeds but not to substantially damage the crop.

17. A method as claimed in claim 16 in which there is used a compound in which $-X$ is $-CF_3$ and in which the herbicide is applied to weeds growing in the presence of corn, rice, cotton or soybeans.

18. A process for preparing a herbicidally active compound as defined in claim 1 which comprises reacting one molar proportion of a compound of the formula:

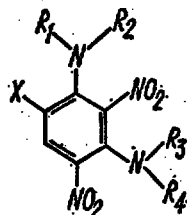


in which X is halogen or trifluoromethyl and Y is a reactive halogen, with two molar proportions of a compound of the formula R_1-NH-R_2 and two molar proportions of a compound of the formula R_3-NH-R_4 , R_1 , R_2 , R_3 and R_4 being as defined in claim 1.

19. A process according to claim 18 in which R_1-NH-R_2 and R_3-NH-R_4 are the same compound and the reaction is effected in one step between one molar proportion of the substituted dinitro-benzene and four molar proportions of the amine.

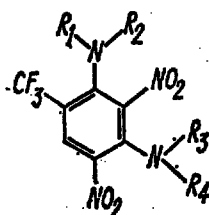
20. A process according to claim 18 in which R_1-NH-R_2 is different from R_3-NH-R_4 and the reaction is effected in two steps, first between the R_3-NH-R_4 and the substituted dinitro-benzene and then between the product of the first step and R_1-NH-R_2 .

21. A herbicidal compound of the formula:



wherein X is a halogen atom or trifluoromethyl group, and each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or aliphatic hydrocarbon group, which may be substituted by a halogen atom, a hydroxy group or an alkoxy group of 1-4 carbon atoms, or R_1 and R_2 together or R_3 and R_4 together are a divalent hydrocarbon group forming the complement to a heterocycle which includes the nitrogen atom as ring member, with the proviso that at least one of said R 's is a said hydrocarbon group, but R_1 and R_2 are both hydrogen atoms when X is a halogen atom.

22. A herbicidal compound according to claim 21 having the formula:



wherein R_1 , R_2 , R_3 and R_4 are each hydrogen, alkyl, alkenyl, or alkynyl, at least one

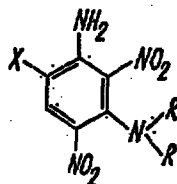
of said R's being a hydrocarbon group, or $R_1 + R_2$ and/or $R_3 + R_4$ represent an alkylene group having 2 to 6 carbon atoms in the chain.

23. A compound according to claim 22 in which R_1 is hydrogen, R_2 and R_3 are each hydrogen or alkyl of 1 to 5 carbon atoms, and R_4 is alkyl of 1 to 5 carbon atoms.

24. A compound according to claim 23 in which the total number of carbon atoms contained in $R_1 + R_2 + R_3 + R_4$ is from 4 to 8.

25. A compound according to claim 23 in which R_1 and R_2 are hydrogen, R_3 is hydrogen or alkyl of 1 to 5 carbon atoms and R_4 is alkyl of 1 to 5 carbon atoms.

26. A herbicidal compound according to claim 21 having the formula:



in which X is halogen and each R is selected from hydrogen and alkyl of 1 to 5 carbon atoms, the total number of carbon atoms represented by $R + R$ being 3 to 8.

27. A compound according to claim 26 in which X is chloro.

28. A compound according to claim 26 in which X is bromo.

29. N^2, N^3 -diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

30. N^2 -(1-methyl-2-methoxyethyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

31. N^1 -ethyl- N^3, N^3 -diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

32. N^3, N^3 -di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

33. N^1 -methyl- N^3, N^3 -diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

34. N^1, N^1 -di-*n*-propyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

35. N^2 -(3-pentyl)-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine.

36. N^3, N^3 -di-*n*-propyl-2,4-dinitro-6-chloro-1,3-phenylenediamine.

37. N^3 -(3-pentyl)-2,4-dinitro-6-chloro-1,3-phenylenediamine.

38. Any of the substituted dinitrophenylenediamines according to claim 21 hereinbefore identified.

39. Substituted dinitrophenylenediamines when prepared by a process according to any of claims 18, 19 or 20.

J. A. KEMP & CO.,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *