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PATENT SPECIFICATION

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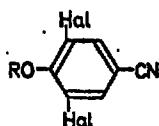
COMPLETE SPECIFICATION

4-Hydroxybenzonitrile Derivatives

We, MAY & BAKER LIMITED, a British Company of Dagenham, Essex, England, 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 benzonitrile derivatives which are useful as herbicides.

As a result of research and experimentation it has been discovered that certain benzonitrile derivatives have valuable herbicidal properties. The benzonitrile derivatives are compounds of the general formula:—



wherein R represents a hydrogen atom or an acetyl group, and Hal represents a halogen atom, the two halogen atoms being identical. The alkali metal, alkaline earth metal, ammonium and amine salts of the compounds of general formula I in which R represents a hydrogen atom also have valuable herbicidal properties; and it is to be understood that where reference is made in this specification to benzonitrile derivatives generally, this term includes, where appropriate, the above-mentioned salts. Particularly suitable amines for the formation of salts are mono-, di- and trimethylamines, mono-, di- and triethanolamines, octylamine, dioctylmethylamine, tri-(3,5,5-trimethylhexyl)amine, tributylamine and morpholine.

Compounds of particular interest are 3,5-diiodo-4-hydroxybenzonitrile and its salts, particularly its salts with alkali metals, especially sodium, alkaline earth metals, especially calcium, ammonia and amines; 3,5-dibromo-

4-hydroxybenzonitrile and its salts, particularly its salts with alkali metals, especially sodium, alkaline earth metals, especially calcium, ammonia and amines; 3,5-diiodo-4-acetoxymethylbenzonitrile; and 3,5-dibromo-4-acetoxymethylbenzonitrile. Of these compounds, 3,5-diiodo-4-hydroxybenzonitrile and its salts, and 3,5-dibromo-4-hydroxybenzonitrile and its salts are especially preferred.

According to one feature of the present invention one or more benzonitrile derivatives of formula I or salts thereof are used to control the growth of weeds, i.e. undesired vegetation. Usually the benzonitrile derivatives are associated with compatible diluents suitable for use in herbicidal compositions, for example as described below.

The benzonitrile derivatives of formula I and salts thereof can be used to control the growth of one or more broad-leaved weeds such as *Ambrosia artemisiifolia*, *Amaranthus retroflexus*, *Atriplex patula*, *Barbarea vulgaris*, *Brassica alba*, *Brassica nigra*, *Capsella bursa-pastoris*, *Convolvulus* species, *Cirsium* species, *Chenopodium album*, *Chrysanthemum segetum*, *Datura stramonium*, *Erysimum cheiranthoides*, *Euphorbia lathyris*, *Galium aparine*, *Matricaria inodora*, *Matricaria chamomilla*, *Portulaca*, *oleraceae*, *Polygonum aviculare*, *Polygonum convolvulus*, *Polygonum lapathifolium*, *Polygonum persicaria*, *Polygonum hydropiper*, *Polygonum scabrum*, *Raphanus raphanistrum*, *Rumex* species, *Spergula arvensis*, *Stellaria media*, *Sonchus* species, *Senecio vulgaris*, *Sinapis arvensis*, *Veronica* species and *Xanthium* species. The amounts of benzonitrile derivative or derivatives applied to the weeds to control their growth vary with the nature of the weeds, the composition applied, the mode and time of application and, when the growth of weeds is to be controlled in the presence of crops, the nature of the crops. In general, taking

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these factors into account, application rates of 0.28 to 0.56 kg per hectare give good results, particularly with the preferred compounds. It must, however, be understood that higher application rates may be used to secure more complete control, particularly of resistant weed species, to the extent that this is consistent with the tolerance of any crops present.

The benzonitrile derivatives of formula I are particularly suitable for application to crop-growing areas. By the term "crop-growing areas" is meant areas on which crops are, or will be, growing. Any diluent used should of course be one that is well tolerated by the crop being treated, and the benzonitrile derivative should be applied at a rate such that the crops do not suffer any substantial permanent damage.

Crops found to be particularly suitable for treatment include graminaceous crops such as grasses, for example *Poa* species, *Festuca* species, *Dactylis* species, *Lolium* species and *Agrostis* species, sugar-cane and cereals, for example wheat, oats, barley, rye, maize, rice, millet and sorghum; legumes such as peas, beans, lucerne (alfalfa) and red and white clovers; flax; linseed; carrots; onions; and cruciferous crops such as kale, rape and cabbage. The amounts of benzonitrile derivative or derivatives of formula I, or salts thereof, applied in the aforesaid treatments vary with the nature of the crop, the composition applied and the mode and time of application. In general, taking these factors into account, it is found that, particularly when using the preferred compounds, crops and crop-growing areas may be treated at rates of up to 0.56 kg. of benzonitrile derivative or derivatives per hectare without risk of substantial permanent damage to the crop, while graminaceous crops in particular may with safety be treated at rates of up to 1.68 kg of benzonitrile derivative or derivatives per hectare.

As will appear from Experiments A to J hereinafter described, many of the benzonitrile derivatives of formula I, and salts thereof, possess a high degree of selective herbicidal activity which renders them particularly useful for the control of weeds, particularly broad-leaved weeds, in crops, particularly the crops hereinbefore listed.

Areas of fallow or uncultivated land can also be treated with one or more benzonitrile derivatives of formula I, or salts thereof, usually in association with one or more diluents compatible with the benzonitrile derivative or derivatives, to control the growth of undesired vegetation. When used for this purpose, in which a total herbicidal effect is frequently desired, the compositions are normally applied at dosage rates higher than those used in the treatment of crops and crop-growing areas in which crops are growing and in the treat-

ment of weeds to control their growth in the presence of crops. The precise dosage rate utilised will depend upon the nature of the vegetation treated and the effect sought, but in general dosage rates of 2.24 to 4.48 kg. of benzonitrile derivative or derivatives of formula I, or salts thereof, per hectare give good results.

In a similar manner to the treatment of fallow or uncultivated land, undesired vegetation growing in crop-growing areas such as plantations, orchards and vineyards may be treated to control its growth by directional application, particularly by directional spraying.

Compositions containing benzonitrile derivatives of formula I and salts thereof can also be used to exercise a desiccant effect on crops such as potatoes, hops, cotton and leguminous seed-crops. For these purposes, application rates of 1.12 to 4.48 kg. of benzonitrile derivatives per hectare give good results.

The invention includes also herbicidal compositions suitable for agricultural use comprising one or more benzonitrile derivatives of formula I, or salts thereof, in association with, and preferably homogeneously dispersed in, one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions. The term "herbicidal compositions suitable for agricultural use" is used in a broad sense to include not only compositions which are ready for use as herbicides, but also concentrates which must be diluted before use. The term "homogeneously dispersed" is used to include compositions in which the benzonitrile derivative is dissolved in the diluent or surface-active agent. Preferably the compositions contain 0.05 to 90% by weight of the benzonitrile derivative or derivatives. The diluent may for example be a liquid which is other than an animal, vegetable or mineral oil and contains a surface-active agent, an adhesive or an additional herbicidally active compound; or an animal, vegetable or mineral oil; or a solid. (The expression "mineral oil" as used herein means an oil of mineral origin having a boiling range essentially above 200° C.).

Certain compositions containing compounds of formula I or alkali metal salts thereof have, however, been disclosed in the literature, more particularly compositions wherein the benzonitrile derivative is a compound of formula I in which

a) Hal represents a chlorine, bromine or iodine atom and R is a hydrogen or acetyl group, and the diluent is a liquid other than an animal oil, a mineral oil (as hereinbefore defined) or a vegetable oil, or

b) Hal represents a chlorine, bromine or iodine atom, R is a sodium ion and the diluent is ethanol or aqueous ethanol, and these compositions are not claimed herein

except when associated with a surface-active agent, an adhesive or another herbicidally active compound.

The herbicidal compositions may contain both a diluent and a surface-active agent, e.g. a wetting, dispersing or emulsifying agent. The surface-active agent may be of the ionic or non-ionic type, for example sulphuricino-leates; quaternary ammonium derivatives; products based on condensates of ethylene oxide, such as condensates of ethylene oxide with nonyl or octyl phenol; fatty acid esters of anhydrosorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide; alkali and alkaline earth metal salts of sulphuric acid esters and sulphonic acids such as sodium di-nonyl and di-octyl sulpho-succinates; and alkali and alkaline earth metal salts of high molecular weight sulphonic acid derivatives such as sodium and calcium ligno-sulphonates.

Examples of suitable solid diluents are aluminium silicate, talc, calcined magnesia, kieselsguhr, tricalcium phosphate, powdered cork, absorbent carbon black, and clays such as kaolin or bentonite. The solid compositions, which may take the form of dusts, granules or wettable powders, are preferably prepared by grinding the benzonitrile derivatives of formula I or salts thereof with the solid diluents or by impregnating the solid diluents with solutions of the benzonitriles in volatile solvents, evaporating the solvents and, if necessary, grinding the products so as to obtain powders. Granular formulations may be prepared by absorbing the benzonitrile derivatives dissolved in volatile solvents onto the solid diluents in granular form and evaporating the solvents, or by granulating compositions in powder form obtained as described above. The wettable powders in particular preferably contain one or more surface-active agents. Wettable powders according to the present invention may be treated with water immediately before use to give suspensions ready for application.

Suitable liquid diluents include aqueous, organic and aqueous organic liquids, for example tetrahydrofurfuryl alcohol, acetophenone, cyclohexanone, isophorone, dimethylformamide, methyl cellulose (the monoethyl ether of ethylene glycol), toluene, xylene and mineral, animal and vegetable oils. ("Cello-solve" is a Registered Trade Mark). Mixtures of these diluents can be used. The liquid compositions may contain a wetting, dispersing or emulsifying agent, e.g. such as those described above, particularly when the liquid diluent is other than an animal, vegetable or mineral oil. Liquid concentrates in the form of solutions, especially of salts, in water-miscible organic solvents which give solutions ready for use on dilution with water are particularly preferred. When desired, the emulsions

of the benzonitrile derivatives of formula I may be used in the form of self-emulsifying concentrates containing the active substances dissolved in the emulsifying agents or in solvents containing emulsifying agents compatible with the active substances, the simple addition of water producing compositions ready for use. Suitable solvents for this purpose include ketones such as cyclohexanone and isophorone. Self-emulsifying concentrates of the types which give rise to water-in-oil emulsions may also be used.

Herbicidal compositions in the form of aerosols containing one or more of the benzonitrile derivatives of formula I or salts thereof are also within the scope of the present invention.

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives. If desired, other herbicidally active compounds may be included in the herbicidal compositions of the present invention such as the phenoxy-alkanoic herbicides, for example MCPB [γ (4-chloro - 2 - methylphenoxy) - butyric acid], 2,4 - DB [γ (2,4 - dichlorophenoxy)butyric acid], MCPA (4 - chloro - 2 - methylphenoxyacetic acid), 2,4 - D (2,4 - dichlorophenoxyacetic acid), CMPP [α (4-chloro - 2 - methylphenoxy)propionic acid] and 2,4 - DP [α (2,4 - dichlorophenoxy)propionic acid]; α,α - dichloropropionic acid; trichloroacetic acid; 3 - amino-1,2,4 - triazole and Barban [4 - chloro-but - 2 - ynyl N - (3' - chlorophenyl) carbamate].

The invention includes also the preparation of herbicidal compositions by a process which comprises mixing, preferably homogeneously dispersing, a benzonitrile derivative of formula I, or a salt thereof, with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions.

Compounds of the general formula I and their alkali metal, alkaline earth metal, ammonium and amine salts, but with the provisos that R does not represent a hydrogen atom, a sodium ion or an acetyl group if Hal represents a chlorine, bromine or iodine atom, and R does not represent a potassium ion if Hal is an iodine atom, have not previously been prepared and are included within the scope of this invention.

In order to demonstrate the valuable properties of the benzonitriles of formula I and salts thereof for herbicidal purposes, the following experiments A to J were carried out. In the experiments, and throughout this specification, the percentages are given on a weight by volume basis, except where otherwise noted, and where rates of application and percentages are given for salts of the benzonitrile derivatives, those rates and percentages are calculated on the basis of the equivalent amount of the

corresponding free phenol, not on the actual amount of the salt. The "Manoxol-N" referred to in the experiments is sodium di-nonyl sulphosuccinate, and the "Ethylan BCP" is an ethylene oxide/alkylphenol condensate. ("Manoxol" and "Ethylan" are Registered Trade Marks.)

Experiments A to E show the excellent tolerance of the indicated crops for the benzonitrile derivatives.

A. Wheat

An experiment was laid out in winter-sown wheat, variety "Capelle". Plots of 0.135 hectare were sprayed with solutions of the potassium salt of 3,5-dibromo-4-hydroxybenzonitrile in water at rates of 0.56 and 1.12 kg in 220 litres of water per hectare, and further plots sprayed with similar solutions containing in addition 0.01% of Manoxol-N in the final spray solution. At the time of treatment the wheat plants in some plots were at the tillering stage with 4 or 6 leaves and in others they were at the jointing stage. When the ears had formed, a visual estimate was made of the heights of plants in each of the treated plots in comparison with untreated plants: no differences could be observed. Detailed examination of plants sampled from the treated plots failed to reveal morphological damage. Subsequently at harvest there were no significant variations in yield between the treated and untreated plots.

B. Barley

An experiment was laid out in spring-sown barley, variety "Rika". Plots of 0.135 hectare were sprayed with solutions of the ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile in water with or without 0.025% Manoxol-N in the final spray solutions at rates of 0.56 and 1.12 kg in 220 litres of water per hectare in some plots and 0.56 and 1.12 kg in 660 litres of water per hectare in others. At the time of application the barley plants were showing 5 to 6 leaves and were producing tillers. Treated and untreated plots were compared when the crop had come into ear and no appreciable damage could be observed in the treated plots. At harvest, the yields from the treated and from untreated plots showed no significant variations.

C. Oats

Plots of oats, variety "Condor", at the 3-4 leaf stage or at the 5-6 leaf tillering stage were sprayed with solutions of the sodium salt of 3,5-diiodo-4-hydroxybenzo-

nitrile at a rate of 1.12 kg in 220 litres of water per hectare with or without 0.025% Manoxol-N in the final spray solution. The crop plants were examined when they were in ear, six weeks after treatment in the case of plots sprayed at the 3 to 4 leaf stage and four weeks after treatment in the case of plots sprayed at the 5 to 6 leaf tillering stage. The heights and vigour of the crops were compared with untreated plots and samples examined for morphological distortion. No reduction in growth nor any other phytotoxic damage was found with any of the treatments and at harvest there were no significant differences in yield between the treated and untreated plots.

D. Lucerne

Plots of seedling lucerne with 2 or 3 trifoliolate leaves were sprayed with solutions of the potassium salt of 3,5-dibromo-4-hydroxybenzonitrile in water, using logarithmically diminishing amounts of the benzonitrile derivative in 198 litres of water per hectare, starting at 1.68 kg per hectare. Seven days afterwards a visual assessment of the crop was made and correlated with the application rate of active ingredient. The highest rate tolerated by the lucerne without visible damage was 1.4 kg per hectare.

The potassium salt of 3,5-dibromo-4-hydroxybenzonitrile can be prepared as follows:

3,5 - dibromo - 4 - hydroxybenzonitrile (12 kg) is dissolved in a mixture of water (211 litres) and aqueous 8.15 N potassium hydroxide solution (5.315 litres) and the solution filtered. Potassium chloride (21.66 kg) is added to the filtrate with stirring and the white crystalline product which separates is collected and dried at 40-60° C giving the potassium salt of 3,5 - dibromo - 4 - hydroxybenzonitrile (13.16 kg, assay as potassium salt 88%).

Proceeding in a similar manner with 3,5-diiodo-4-hydroxybenzonitrile the corresponding potassium salt is obtained as a white solid (assay as potassium salt 94%).

E. Peas

Plots of peas, variety "Kelvedon Wonder", were sprayed when 15 cms high with various amounts of the sodium salt of 3,5-diiodo-4-hydroxybenzonitrile in 220 litres of water per hectare, with or without Manoxol-N as indicated. After seven days, a visual estimate of phytotoxicity was made, giving the following results:—

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Rate of Application (kg/hectare)	Amount of Manoxol-N (%)	Phytotoxicity
0.56	0	negligible
1.12	0	negligible
0.56	0.01	negligible
1.12	0.01	negligible
0.56	0.025	slight leaf scorch
1.12	0.025	slight leaf scorch and chlorosis

No permanent damage was produced in any of the plots and in each case the plants recovered and produced a satisfactory crop of peas.

5 Experiments F and G show the herbicidal effect of the benzonitrile derivatives on weeds. F.

10 Seedlings (20 per plot) of various weed species growing in pots in a greenhouse were sprayed with aqueous acetone solutions of a number of benzonitrile derivatives of formula

I, the control specimens being sprayed with aqueous acetone. The concentrations of the solutions were so arranged that they corresponded with field application rates of 0.14, 0.28, 0.56 and 1.12 kg. per hectare of benzonitrile derivative when sprayed by the experimental laboratory spray machine in 440 litres of solution per hectare. The minimum rates at which each weed species was killed completely are set out in the following table:

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Weed Species	Benzonitrile Derivative (minimum effective dose in kg/hectare)					
	3,5-dichloro-4-hydroxybenzonitrile	3,5-dichloro-4-acetoxybenzonitrile	3,5-dibromo-4-hydroxybenzonitrile	3,5-dibromo-4-acetoxybenzonitrile	3,5-diiodo-4-hydroxybenzonitrile	3,5-diiodo-4-acetoxybenzonitrile
<i>Centaurea cyanus</i>	<0.14	<0.14	<0.28	<0.14	<0.14	<0.14
<i>Chenopodium album</i>	<0.14	>1.12	<0.28	<0.14	<0.14	<0.14
<i>Polygonum lapathifolium</i>	<0.14	0.14—0.28	<0.28	<0.14	<0.14	—
<i>Raphanus raphanistrum</i>	<0.14	0.56—1.12	<0.28	<0.14	0.14	<0.14
<i>Sinapis arvensis</i>	<0.14	<0.14	<0.28	<0.14	<0.14	<0.14
<i>Chrysanthemum segetum</i>	<0.14	0.14—0.28	<0.28	<0.14	0.14	<0.14
<i>Galium aparine</i>	>1.12	>1.12	—	0.56—1.12	0.14—0.28	—
<i>Matricaria inodora</i>	<0.14	0.28	<0.28	<0.14	<0.14	<0.14
<i>Stellaria media</i>	>1.12	>1.12	0.28—0.56	0.56—1.12	<0.14	<0.14

- G. The effects of adding various proportions of a wetting agent, Manoxol-N, to aqueous solutions of the ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile and the sodium salt of 3,5-diiodo-4-hydroxybenzonitrile were examined by experiments carried out in the greenhouse on weed species, *Chenopodium album* (2 to 3 pairs of leaves), *Raphanus raphanistrum* (1 to 2 leaves), *Matricaria inodora* (3 to 4 leaves) and *Stellaria media* (5 to 6 pairs of leaves), found in Experiment F to be less susceptible. In these experiments 20 seedlings of each weed species were sprayed at rates equivalent to field application rates of 0.07, 0.14, 0.28 and 0.56 kg of the benzonitrile derivative per hectare in 418 litres of solution per hectare. The mortalities produced by various rates of application are expressed in the following table as a percentage of the survival figures of unsprayed control seedlings.

Ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile

%age kill of weeds

5-diiodo- 4-acet- ylbenzo- nitrile	Amount of Manoxol-N (%)	Rate of Appli- cation (kg/hectare)	%age kill of weeds			
			<i>Chenopo- dium al- bum</i>	<i>Raphanus raphani- strum</i>	<i>Matrica- ria ino- dora</i>	<i>Stellaria media</i>
<0.14	0	0.07	0	13	7	—
	0	0.14	0	13	53	—
<0.14	0	0.28	13	40	93	—
—	0	0.56	73	87	100	—
	0.01	0.07	0	0	27	—
<0.14	0.01	0.14	60	0	80	—
<0.14	0.01	0.28	87	93	93	—
	0.01	0.56	93	87	100	—
<0.14	0.025	0.07	27	33	60	—
	0.025	0.14	60	66	93	—
—	0.025	0.28	93	93	93	—
<0.14	0.025	0.56	87	100	100	—
	0.05	0.07	67	13	73	—
<0.14	0.05	0.14	80	73	100	—
	0.05	0.28	93	86	100	—
	0.05	0.56	100	100	93	—

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Sodium salt of 3,5-diiodo-4-hydroxybenzonitrile

Amount of Manoxol-N (%)	Rate of Appli- cation (kg/hectare)	%age kill of weeds			
		<i>Chenopo- dium al- bum</i>	<i>Raphanus raphani- strum</i>	<i>Matrica- ria ino- dora</i>	<i>Stellaria media</i>
0	0.07	0	0	0	0
0	0.14	7	27	27	0
0	0.28	13	20	40	27
0	0.56	0	67	60	33
0.01	0.07	0	27	67	0
0.01	0.14	53	73	93	80
0.01	0.28	93	87	93	93
0.01	0.56	93	100	93	93
0.025	0.07	40	67	60	27
0.025	0.14	80	100	93	67
0.025	0.28	100	100	100	87
0.025	0.56	100	100	100	87
0.05	0.07	47	80	87	13
0.05	0.14	100	80	93	33
0.05	0.28	100	93	100	80
0.05	0.56	100	100	100	93

H.

This experiment shows the effectiveness of the benzonitrile derivatives in controlling the growth of weeds in crops of wheat. In order to compare the application rates of benzonitrile derivatives required to control the growth of weeds in crops of wheat and the application rates tolerated by the crops under field conditions, plots of spring-sown wheat, variety "Jufy", at the 7-leaf stage, containing a natural weed population, were sprayed with a range of solutions containing various concentrations of benzonitrile derivatives of formula I, or salts thereof. The spray solutions were obtained by diluting liquid concentrates with water, 198 litres of water per hectare being used for each solution. The application rate of each benzonitrile derivative was decreased

logarithmically from 1.68 kg. to 0.21 kg. per hectare. The plots were examined 6 days after spraying to determine the maximum application rates tolerated by the wheat plants (taken as the minimum application rates giving slight leaf-scorch) and after 25 days to determine the minimum concentration giving complete weed control. The main weed species present throughout the plots, and which were at various stages of growth from young to flowering plants, were *Veronica* species, *Senecio vulgaris*, *Sinapis arvensis*, *Sonchus* species, *Chenopodium album*, *Polygonum aviculare*, *Polygonum persicaria*, *Polygonum lapathifolium*, *Matricaria* species and *Stellaria media*.

The results obtained are given in the following table:

Composition diluted to give spray solutions	Minimum application rate in kg/hectare of benzonitrile derivative giving complete weed control after 25 days		Crop tolerance (slight-leaf scorch) after 6 days. Maximum Application Rate (kg/hectare)
	General	<i>Stellaria media</i> & <i>Veronica</i> species	
An emulsifiable concentrate of 3,5-diiodo-4-hydroxybenzonitrile (10% w/v), Ethylan BCP (5% w/v) and dimethylformamide (to 100% by volume)	0.28	0.28—0.63	1.26—1.68
A solution of the ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile (20% w/v) in tetrahydrofurfuryl alcohol	0.21—0.42	0.56—0.7	0.84—0.98
An emulsifiable concentrate of 3,5-diiodo-4-acetoxybenzonitrile (10% w/v), Ethylan BCP (5% w/v) and dimethylformamide (to 100% by volume)	0.28—0.35	0.49	1.68

Damage to the wheat plants was in each case superficial and temporary.

I.

- 5 Experiment I shows the effect on weed control of incorporating a wetting agent. In field experiments plots of winter-sown wheat, variety "Capelle", were sprayed, when the natural weed population was at the seedling or young plant stage of growth, with solutions

of the sodium salt of 3,5-diiodo-4-hydroxybenzonitrile in water at rates of 0.42 and 0.84 kg. in 198 litres of water per hectare. Other plots were sprayed with similar solutions containing in addition 0.025% Manoxol-N. The weed control of the various compositions was determined by counting the number of weed species surviving in two 0.4 m² quadrat counts taken in each plot. The following results were obtained.

Amounts of Manoxol-N (%)	Rate of Application (kg/hectare)	<i>Atriplex patula</i>	<i>Polygonum aviculare</i>	<i>Polygonum convolvulus</i>
0	0.42	19	63	7
0.025	0.42	10	35	12
0	0.84	3	43	4
0.025	0.84	9	16	6
Unsprayed control	—	112	228	122

J.

- 25 Experiment J demonstrates the effectiveness of the treatment of crops with compositions containing one or more benzonitrile derivatives of formula I, or salts thereof, in association with one or more diluents compatible with the benzonitrile derivatives, to

produce desiccation. The experiment shows the destruction of Potato haulm.

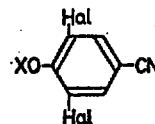
A crop of potatoes, variety "Majestic", in full leaf growth and in flower, was sprayed with solutions prepared by diluting the following concentrates with water.

- (a) the ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile (40% w/v) in solution in tetrahydrofurfuryl alcohol: 15
- (b) the ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile (40% w/v) in solution in tetrahydrofurfuryl alcohol, and
- (c) the potassium salt of 3,5-dibromo-4-hydroxybenzonitrile (4% w/v) in solution in water. 20
- 10 Application was made at a constant rate of 198 litres per hectare of solution through a spraying machine giving continuous dilution 25

Minimum effective dose giving complete kill
(kg/hectare)

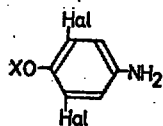
Compound	0.025% wetting agent	0.05% wetting agent
Ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile	1.26	1.47
Ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile	1.05	1.19
Potassium salt of 3,5-dibromo-4-hydroxybenzonitrile	1.68	1.68

- 30 The benzonitrile derivatives of formula I and, where appropriate, salts thereof, may be prepared by the following processes. The expression "lower" when used herein in relation to alkyl and acyl groups indicates that the group in question contains at most 4 carbon atoms.



III

- 35 I. When R represents a hydrogen atom.
(i) By the diazotisation of an aniline derivative of general formula:



II

- 40 (wherein Hal represents a halogen atom, the two halogen atoms being the same, and X represents a hydrogen atom, a lower alkyl group which may be unsaturated, an alkoxy-alkyl group, a lower carboxylic acyl group or a benzyl group) and conversion of the
- 45 diazonium salt into a benzonitrile derivative of general formula:

(wherein the various symbols are as defined above) by treatment with sodium or potassium cupro- or nickelo-cyanide or potassium (or sodium) cyanide followed by

(a) when X represents a lower alkyl or an alkoxyalkyl group, dealkylation by treatment with aluminium trichloride or pyridine hydrochloride;

(b) when X represents an unsaturated alkyl group, hydrogenolysis;

(c) when X represents an alkoxymethyl group, acid hydrolysis, which must be carried out under mild conditions to avoid simultaneous hydrolysis of the cyano group;

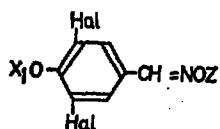
(d) when X represents a lower carboxylic acyl group, by deacylation by known methods such as hydrolysis, transesterification by treatment with a suitable alcohol, for example ethanol, under acid conditions; or aminolysis by treatment with a suitable amine, for example diethanolamine, in an

alcohol, for example ethanol. Hydrolysis, which must be carried out under mild conditions to avoid simultaneous hydrolysis of the cyano group, is preferably carried out under alkaline conditions by boiling for a short time with dilute aqueous or alcoholic, preferably ethanolic, sodium hydroxide solution; and

(c) when X represents a benzyl group, hydrogenolysis or acid hydrolysis.

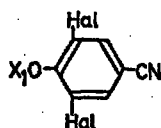
The compounds of formula II which serve as starting materials in this process may be prepared by known methods. By the term "known methods" as used in the present specification is meant methods heretofore used or described in the literature.

(ii) by conversion of an oxime of general formula:



IV

[wherein X₁ represents a hydrogen atom or a lower alkyl or acyl group, Z represents a hydrogen atom or an acyl group and Hal is as defined above] by known methods to give a benzonitrile derivative of general formula:

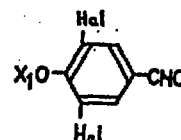


V

(wherein the various symbols are as hereinbefore defined), such as treatment with an acid anhydride, for example acetic anhydride (compounds of formula V wherein X₁ represents an acyl group being obtained when X₁ in formula IV represents a hydrogen atom) [as described by Auwers and Reis, Ber. 29 (2), 2355—2360 (1896) for the preparation of 3,5-dichloro-, 3,5-dibromo- and 3,5-diiodo-acetoxybenzonitrile], thionyl chloride, phosphorus pentoxide or vapour phase dehydration. When X₁ in the formula V represents a lower alkyl or acyl group, this is followed by dealkylation or deacylation by known methods such as those mentioned above in A (i) (as described by Auwers and Reis, *loc. cit.*, for the hydrolysis of 3,5-dichloro, 3,5-dibromo- and 3,5-diiodoacetoxybenzonitrile to the corresponding hydroxybenzonitrile by use of alcoholic sodium hydroxide solution). The conversion of an oxime of formula IV to a benzonitrile derivative of formula V is pre-

ferably effected with thionyl chloride or acetic anhydride, followed by hydrolysis where necessary.

The oximes of general formula IV may be prepared by reacting a benzaldehyde derivative of general formula:



VI

(wherein the various symbols are as defined above) with hydroxylamine. The hydroxylamine may be introduced in the form of the hydrochloride, reaction being preferably carried out in the presence of a base, or may be formed *in situ* by the treatment of sodium carbonate or bicarbonate and sodium nitrite with sulphur dioxide, followed by hydrolysis.

The benzaldehyde derivatives of formula VI may be prepared by known methods such as that described by Auwers and Reis [Ber. (1896), 29 (2), 2355].

(iii) By the halogenation of 4-cyanophenol.

Halogenation may be effected by known methods, e.g. with molecular hydrogen in organic solvents such as chloroform, acetic acid or ethanol as described by Berg and Newberry (J. Chem. Soc., 1949, p. 642) optionally in the presence of a catalyst such as ferric chloride, with potassium or sodium chlorate in the presence of hydrochloric acid, sodium or potassium hypobromite or with a mixture of sulphur monochloride, sulphuryl chloride and aluminium chloride. Iodination is preferably effected with a mixture of sodium or potassium iodide and sodium or potassium iodate in aqueous solution, or with iodine monochloride in a suitable solvent such as glacial acetic acid, complete utilisation of iodine being obtained by these processes. Iodination may also be effected with an alkali metal iodide in the presence of an oxidising agent.

Halogenation may also be effected upon an acyl derivative of 4-cyanophenol, such as 4-acetoxybenzonitrile, halogenation being accompanied by simultaneous deacylation to give a 3,5-dihalo-4-hydroxybenzonitrile.

(II) When R represents an acetyl group:

By the acetylation of the corresponding 4-hydroxybenzonitrile of general formula I in which R represents a hydrogen atom. The acetylation may be effected according to known methods, for example by:

(i) reaction with acetic anhydride in the presence of a small amount of a condensing agent such as concentrated sulphuric acid or

reaction with acetic anhydride and an alkali metal, such as sodium or potassium, acetate.

- (ii) Reaction with an acetyl halide, for example acetyl chloride, in the presence of a tertiary base, such as pyridine, or in the presence of a quaternary ammonium salt such as tetralkylammonium halide, for example tetramethylammonium chloride. When pyridine is used as a condensing agent it may also act as a solvent for the reactants.

(iii) By reaction with isopropenyl acetate in the presence or absence of acetic acid.

III Salts of benzonitrile derivatives of general formula I wherein R represents a hydrogen atom:

- Salts with alkali metals, alkaline earth metals, ammonia and amines may be prepared by treating the benzonitrile derivative of general formula I with a stoichiometric quantity of an alkali metal or alkali metal alkoxide, hydroxide, carbonate or bicarbonate, an alkaline earth metal hydroxide, ammonia or ammonium hydroxide or an amine, in a suitable solvent such as water or a lower aliphatic alcohol for example methanol or ethanol or mixtures thereof.

Preferred methods are:—

- A. For alkali metal salts, by (i) dissolving the 4-hydroxybenzonitrile in an aqueous solution containing a slight excess of the alkali metal hydroxide, carbonate or bicarbonate and precipitating the salt from solution by salting out by the addition of the appropriate alkali metal halide, for example, the chloride.

- (ii) treatment of the 4-hydroxybenzonitrile of formula I with a stoichiometric quantity of the alkali metal alkoxide in the corresponding alcohol (e.g. sodium methoxide in methanol or sodium ethoxide in ethanol). In some cases the salt may separate from the alcoholic mixture and can be collected by filtration. Alternatively, the alkali metal salt may be isolated by evaporation of the solvent.

- B. for alkaline earth metal salts of the 4-hydroxybenzonitrile of formula I, which are sparingly soluble in water; by treatment of an aqueous solution of a soluble salt, for example, an alkali metal salt, with an aqueous solution of a soluble alkaline earth metal salt. For example, calcium salts of the 4-hydroxybenzonitriles of formula I, may be prepared by treatment of an aqueous solution of the corresponding sodium salt with an aqueous solution of calcium chloride.

C. For salts with ammonia and volatile amines; by treatment of a suspension of the 4-hydroxybenzonitrile in ethanol with an excess of a solution of ammonia or the volatile

amine in ethanol. The salt separates from the mixture and may be collected by filtration.

D. For salts with non-volatile amines, by mixing equivalent amounts of the 4-hydroxybenzonitrile and the amine in methanol and evaporating the solvent.

The invention is illustrated by the following examples. Examples I to XII show the preparation and use of herbicidal compositions containing benzonitrile derivatives of general formula I and salts thereof, and Examples XIII to XIX show the preparation of new salts of compounds of general formula I (as also do Examples XI and XII). In the Examples the Texofor FN 11 referred to is an ethylene oxide/nonyl phenol condensate, the Texofor F 60 is also an ethylene oxide/octylphenol condensate, the Celite X 205 is finely divided aluminium silicate and the Ethylan BCP is an ethylene oxide/alkylphenol condensate. ("Texofor" and "Celite" are Registered Trade Marks.)

EXAMPLE I.

An emulsifiable concentrate is prepared from the following:

3,5-dichloro-4-hydroxybenzonitrile	20 g
Texofor FN 11	15 g
Isophorone	q.s.p. 100 cc.

by dissolving the 3,5-dichloro-4-hydroxybenzonitrile with heating in a mixture of the Texofor FN 11 and the isophorone. This concentrate is diluted with water and applied to cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds such as *Sinapis arvensis*, *Raphanus raphanistrum*, *Chenopodium album* and *Chrysanthemum segetum* without substantial damage to the crops.

The 3,5-dichloro-4-hydroxybenzonitrile was prepared by the following procedures:

1. A solution of potassium chlorate (8.2 g) in water (110 cc) at laboratory temperature is added dropwise to a stirred suspension of 4-hydroxybenzonitrile (11.9 g) in a mixture of concentrated hydrochloric acid (410 cc) and water (140 cc): an exothermic reaction takes place, the temperature of the reaction mixture rising to about 35° C. When the addition is complete, stirring is continued for 45 minutes. The insoluble solid is then filtered off and crystallised from water, giving 3,5-dichloro-4-hydroxybenzonitrile (8.5 g) as a white solid, m.p. 144—145° C.

2. A mixture of sulphur monochloride (0.2 cc) and sulphurylchloride (21.4 cc) is added to a mixture of 4-hydroxybenzonitrile (11.9 g) and aluminium chloride (0.5 g) and heated under reflux on a steam bath for 1.5 hours.

- The reaction mixture is then evaporated to dryness on the steam bath and the solid residue treated with ice (30 g) and excess concentrated hydrochloric acid (60 cc). The resulting solid is collected, washed with water (20 cc) and recrystallised from ethanol (15 cc) to give a solid product (6 g), m.p. 125—127° C. A second crop of solid product (6 g), m.p. 115—119° C. is obtained by dilution of the mother liquors with water (15 cc). The two crops are combined and treated with a mixture of sodium bicarbonate (5.75 g) and water (20 cc). When effervescence has ceased, the solid product is collected and triturated with water (20 cc). The insoluble solid is collected, dissolved in water (500 cc) and the solution filtered and acidified with hydrochloric acid. The precipitated solid is collected, washed with water (20 cc) and dried at 40° C for 4 hours giving crude 3,5-dichloro-4-hydroxybenzonitrile (7 g), m.p. 140—145° C after softening above 125° C. (melting point unaltered by admixture with an authentic sample of 3,5-dichloro-4-hydroxybenzonitrile), which is recrystallised from ethanol (5 cc) giving 3,5-dichloro-4-hydroxybenzonitrile (2.5 g) m.p. 145—147° C (melting point unaltered by admixture with an authentic sample of 3,5-dichloro-4-hydroxybenzonitrile, m.p. 147—148° C. but depressed by admixture with an authentic sample of 3-chloro-4-hydroxybenzonitrile, m.p. 150—151° C).
3. 4-Hydroxybenzonitrile (200 g) is dissolved in glacial acetic acid (500 cc) with the aid of slight warming to 30—35° C and ferric chloride (0.5 g) added as catalyst. Chlorine is passed into the solution at 45—50° C. for 4—4½ hours until the theoretical increase in weight (116 g) is obtained. The reaction mixture is then cooled to 5—10° C, giving a first crop of 3,5-dichloro-4-hydroxybenzonitrile (207.6 g) m.p. 144—146° C. (melting point unaltered on admixture with an authentic sample of 3,5-dichloro-4-hydroxybenzonitrile, m.p. 144—147° C), which is collected by filtration and dried at 40° C. for 24 hours. The filtrate, on pouring into water (5 litres) and recrystallisation of the resultant solid product, yields further crop of 3,5-dichloro-4-hydroxybenzonitrile (16.6 g), m.p. 144—145° C.

EXAMPLE II.

- An emulsifiable concentrate is prepared from the following:

3,5-dibromo-4-hydroxybenzonitrile	20 g
Texofor FN 11	15 g
Cyclohexanone	q.s.p. 100 g

- as described in Example I. This concentrate is diluted with water and applied to cereals and forage grasses at a rate of 0.56 kg. of

benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds such as *Stellaria media*, *Polygonum lapathifolium*, *Matricaria inodora*, and *Sinapis arvensis* without substantial damage to the crops.

The 3,5-dibromo-4-hydroxybenzonitrile was prepared by the following procedures:—

1. A solution of bromine (128 g) in glacial acetic acid (100 cc) is added, dropwise, to a stirred solution of 4-hydroxybenzonitrile (48 g) in glacial acetic acid (200 cc); an exothermic reaction occurs, the temperature of the reaction mixture rising to about 35° C. When the addition is complete, the mixture is stirred for 3 hours and then added to ice (2 kg). The resulting white solid is collected, washed with water, dried and crystallised from benzene (1.5 litres) giving 3,5-dibromo-4-hydroxybenzonitrile (67 g) as a white solid, m.p. 190—192° C.

2. Bromine (4.13 litres) is added over 45—60 minutes to a stirred mixture of ice (61.2 kg) and a solution of sodium hydroxide (7.2 kg) in water (20 litres) so that the temperature does not exceed 4° C. Excess ice (3.4 kg) is filtered off, giving a 1.12 molar solution of sodium hypobromite.

Water (79 litres), ice (5 kg) and 4-hydroxybenzonitrile (4 kg) are added successively to a stirred solution of sodium hydroxide (1.35 kg) and water (2.5 litres) and stirring is continued until all the 4-hydroxybenzonitrile has dissolved. Sodium hypobromite solution (prepared as described above; 60 litres) is then added, with stirring, to the temperature rising to a maximum of 17.5° C. Shortly after completion of the addition, the starch-iodide test for the presence of hypobromite is found to be negative and further sodium hypobromite solution (12 litres=20% excess) is added. Stirring is continued for a further 3 hours and at the end of this period a slight excess of hypobromite remains. Sodium chloride (40.8 g) is then added and the mixture stirred for 1 hour. The sodium salt of 3,5-dibromo-4-hydroxybenzonitrile which has separated is collected on a pan filter and the moist product dissolved in water (340 litres) at 25° C. The solution is acidified with concentrated hydrochloric acid and the precipitate collected on a pan filter, washed with water until free of chloride ions and dried at 60° C, giving 3,5-dibromo-4-hydroxybenzonitrile (7.31 kg), m.p. 189—192° C.

EXAMPLE III.

- An emulsifiable concentrate is prepared from the following:

3,5-diiodo-4-hydroxybenzonitrile	4% (w/v)
Emcol H 88	10% (w/v)
Solvent D	q.s.p. 100% by volume

by dissolving the 3,5-diiodo-4-hydroxybenzonitrile with heating in a mixture of the Solvent

D and Emcol H 88. [Solvent D is a distillate of coal tar having a density of 1.02, a refractive index of 1.61, a boiling range of 210° to 270° C and a Kauri butanol value of 88 (benzene—100)]. ["Emcol" is a Registered Trade mark.]

A water-soluble concentrate is prepared from the following:—

10	3,5-diiodo-4-hydroxybenzonitrile	4% (w/v)
	Manoxol-N	10% (w/v)
	Diethylene glycol monobutyl ether	
		q.s.p. 100% by volume

by dissolving the 3,5-diiodo-4-hydroxybenzonitrile with heating in a mixture of the ether and Manoxol-N.

These two concentrates are diluted with water and applied to potatoes at a rate of 1.12 kg of benzonitrile derivative in 330 litres of water per hectare to destroy potato haulm.

EXAMPLE IV.

An emulsifiable concentrate is prepared from the following:

25	3,5-diiodo-4-acetoxybenzonitrile	10% (w/v)
	Ethylan BCP	5% (w/v)
	Dimethylformamide	
		q.s.p. 100% by volume

by dissolving the 3,5-diiodo-4-acetoxybenzonitrile with heating in a mixture of the Ethylan BCP and the dimethylformamide. This concentrate is diluted in water and applied to cereal crops, forage grasses and legumes, at a rate of 0.56 kg of benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds without substantial damage to the crops.

Similar emulsifiable concentrates may be prepared by replacing the 3,5-diiodo-4-acetoxybenzonitrile with a similar quantity of 3,5-dichloro-4-acetoxybenzonitrile or 3,5-dibromo-4-acetoxybenzonitrile.

The 3,5-diiodo-4-acetoxybenzonitrile was prepared by the following procedures:

(1) A mixture of 3,5-diiodo-4-hydroxybenzaldehyde (Auwers and Reis, *loc. cit.*) (8.87 g) and acetic anhydride (15 cc) is heated under reflux for 4 hours and then cooled. The crystalline product is filtered off and dissolved in boiling ethanol (100 cc) by the dropwise addition of acetone. The hot solution is treated with charcoal (0.1 g), filtered and cooled to give 3,5-diiodo-4-acetoxybenzonitrile (3.8 g) in the form of fine white crystals, m.p. 204° C.

(2) A mixture of 3,5-diiodo-4-hydroxybenzonitrile (222 g), acetic anhydride (336 cc) and concentrated sulphuric acid (0.5 cc) is heated under reflux for 2 hours and then cooled. The crystalline solid material is filtered

off, washed with ethanol (100 cc) and dried at 60° C to give 3,5-diiodo-4-acetoxybenzonitrile (231 g), m.p. 205—207° C.

(3) 3,5-Diiodo-4-hydroxybenzonitrile (9 g) is suspended in isopropenyl acetate (50 cc), the mixture heated on a steam bath for 3 hours and then allowed to cool. The crystalline product is filtered off and dried in a desiccator, giving, 3,5-diiodo-4-acetoxybenzonitrile (8 g) m.p. 204—206° C.

(4) 3,5-Diiodo-4-hydroxybenzonitrile (18.5 g) is suspended in glacial acetic acid (100 cc) and toluene-*p*-sulphonic acid (1 g) added followed by isopropenyl acetate (25 cc) in one portion. The mixture is heated on a steam bath for 5 hours, allowed to cool, the crystalline product filtered off and dried in an oven at 60° C, giving 3,5-diiodo-4-acetoxybenzonitrile (14.5 g) m.p. 205—207° C.

EXAMPLE V.

An emulsifiable concentrate is prepared from the following:

85	3,5-dibromo-4-hydroxybenzonitrile	10% w/v
	Ethylan BCP	5% w/v
	Isophorone	
		q.s.p. 100% by volume

by dissolving the 3,5-dibromo-4-hydroxybenzonitrile with heating in a mixture of the Ethylan BCP and the isophorone. This concentrate is diluted with water and applied to cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to kill control broad-leaved weeds without substantial damage to the crop.

A similar emulsifiable concentrate may be prepared by replacing the 3,5-dibromo-4-hydroxybenzonitrile by a similar quantity of 3,5-dichloro-4-hydroxybenzonitrile.

EXAMPLE VI.

A concentrated aqueous solution of the sodium salt of 3,5-diiodo-4-hydroxybenzonitrile is prepared by dissolving the benzonitrile derivative salt (10% w/v) and sodium dioctylsulphosuccinate (2% w/v) in water to 100% by volume and is applied after dilution with water at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to cereal crops, forage grasses and peas to control broad-leaved weeds at stages up to flowering, without substantial damage to the crop.

Similar aqueous solutions may be prepared from mixtures of sodium dioctylsulphosuccinate with other alkali metal or amine salts, particularly diethanolamine and triethanolamine salts, of 3,5-diiodo-4-hydroxybenzonitrile and also with alkali metal, and amine salts, particularly diethanolamine and triethanolamine salts, of 3,5-dichloro-4-hydroxybenzonitrile and 3,5-dibromo-4-hydroxybenzonitrile.

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The sodium salt of 3,5-diiodo-4-hydroxybenzonitrile can be prepared as follows. 3,5-Diiodo-4-hydroxybenzonitrile (9.46 kg.) is dissolved in a mixture of water (51 litres) and aqueous N sodium hydroxide solution (25.5 litres) and the solution obtained filtered. Sodium chloride (14 kg.) is added to the filtrate with stirring and the white crystalline product which separates is collected and dried in air at room temperature (20° C.), giving the hydrated sodium salt of 3,5-diiodo-4-hydroxybenzonitrile (10.75 kg; assay as sodium salt 86%). Proceeding in a similar manner with 3,5-dibromo-4-hydroxybenzonitrile, the corresponding sodium salt is obtained as a white solid (assay as sodium salt 82%).

EXAMPLE VII.

A concentrate is prepared from the following:

Ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile 40% w/v
Sodium dioctylsulphosuccinate 4% w/v
Tetrahydrofurfuryl-alcohol q.s.p. 100% by volume

by mixing a solution of the salt in tetrahydrofurfuryl alcohol with a solution of the sodium dioctylsulphosuccinate in tetrahydrofurfuryl alcohol. This concentrate is diluted with water and applied to cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water to control broad-leaved weeds such as *Sinapis arvensis*, *Chenopodium album*, *Matricaria inodora*, *Chrysanthemum segetum*, *Veronica* species and *Polygonum* species without substantial damage to the crops.

Similar concentrates may be prepared by replacing the ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile by a similar quantity of an amine salt of 3,5-diiodo-4-hydroxybenzonitrile or by an ammonium or amine salt of 3,5-dichloro-4-hydroxybenzonitrile.

EXAMPLE VIII.

A liquid concentrate is prepared from the following:

Calcium salt of 3,5-diiodo-4-hydroxybenzonitrile 30% w/v
Ethylan BCP 10% w/v
Cyclohexanone to 100% by volume

This concentrate is diluted with water and sprayed at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare on cereal crops, forage legumes and forage grasses, linseed and flax to control broad-leaved weeds without substantial damage to the crop.

EXAMPLE IX.

Sodium di-nonylsulphosuccinate (4% w/v) is added to a solution of the ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile (20% w/v) in tetrahydrofurfuryl alcohol (prepared as hereinafter described in Example XI) to give a concentrate suitable for use, after dilution with water, in the treatment of seedling lucerne, cereal crops and forage grasses at a rate of 0.56 kg. of benzonitrile derivative in 220 litres of water per hectare to control broad-leaved weeds without substantial permanent damage to the crop.

EXAMPLE X.

Sodium di-nonylsulphosuccinate (4% w/v) is added to a solution of the diethanolamine salt of 3,5-dichloro-4-hydroxybenzonitrile (20% w/v) in tetrahydrofurfuryl alcohol (prepared as hereinafter described in Example XII) to give a concentrate suitable for use, after dilution with water, in the treatment of cereal crops and forage grasses at a rate of 0.56—0.84 kg. in 330 litres of water per hectare to control broad-leaved weeds without substantial damage to the crops.

Examples XI and XII illustrate the preparation of liquid concentrates containing salts of 4-hydroxybenzonitrile derivatives of general formula I with ammonia and amines, which concentrates, after dilution with water are suitable for use as herbicides. A 5 to 10% excess of the amine is usually employed but when the solvent is miscible with water a larger excess may be used to ensure that a clear solution is obtained on dilution with water.

EXAMPLE XI.

A solution having the following composition:

3,5-diiodo-4-hydroxybenzonitrile 2.7 kg
Ammonia (gas) 130 g.

Tetrahydrofurfuryl alcohol q.s. to give 15.6 kg. of solution is prepared by dissolving ammonia gas in part of the tetrahydrofurfuryl alcohol and reacting it with a solution of 3,5-diiodo-4-hydroxybenzonitrile in tetrahydrofurfuryl alcohol. Further tetrahydrofurfuryl alcohol is then added to make the final total weight up to 15.6 kg. These quantities give a 20% w/v solution of the ammonium salt, which yields a clear solution of the ammonium salt on twenty-fold dilution with water. A 40% w/v solution of the ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile can also be prepared by this procedure.

Proceeding in a similar manner, a liquid concentrate containing the ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile is prepared from the following materials:

- 5 3,5-dibromo-4-hydroxybenzonitrile 2.7 kg
Ammonia (gas) 174 g
Tetrahydrofurfuryl alcohol
q.s. to give 15.74 kg of solution.

Similarly 20% w/v solutions of these two ammonium salts may be prepared in 2-methoxyethanol as solvent.

- 10 **EXAMPLE XII.**
Proceeding as described in Example XI, but starting with an amine instead of the ammonia, solutions of the following salts of the 4-hydroxybenzonitrile of formula I are prepared:

- 15 (i) Diethanolamine salt of 3,5-diiodo-4-hydroxybenzonitrile from
(a)
3,5-diiodo-4-hydroxybenzonitrile 25 g
20 diethanolamine 7.1 g
2-methoxyethanol
q.s. to give 125 cc solution

and (b)

- 25 3,5-diiodo-4-hydroxybenzonitrile 25 g
diethanolamine 12 g
tetrahydrofurfuryl alcohol
q.s. to give 125 cc of solution.

- 30 (ii) Diethanolamine salt of 3,5-dibromo-4-hydroxybenzonitrile from
(a)
3,5-dibromo-4-hydroxybenzonitrile 25 g
35 diethanolamine 9.5 g
2-methoxyethanol
q.s. to give 125 cc of solution.

(b)

- 40 3,5-dibromo-4-hydroxybenzonitrile 25 g
diethanolamine 19 g (100% excess)
tetrahydrofurfuryl alcohol
q.s. to give 125 cc of solution.

- 45 (iii) Diethanolamine salt of 3,5-dichloro-4-hydroxybenzonitrile from
3,5-dichloro-4-hydroxybenzonitrile 226 g
diethanolamine 139 g
tetrahydrofurfuryl alcohol
50 q.s. to give 1.21 litres of solution.

- (iv) Triethanolamine salt of 3,5-dibromo-4-hydroxybenzonitrile from

- 3,5-dibromo-4-hydroxybenzonitrile 20 g
triethanolamine 10.8 g
water q.s. to give 50 cc of solution. 55

- (v) N-methyl-di-n-octylamine salt of 3,5-diiodo-4-hydroxybenzonitrile from

- 3,5-diiodo-4-hydroxybenzonitrile 10 g
N-methyl-di-n-octylamine 6.87 g
cyclohexanone
q.s. to give 50 cc of solution. 60

- (vi) Tri-(3,5,5-trimethylhexyl)amine salt of 3,5-diiodo-4-hydroxy benzonitrile from 65

- 3,5-diiodo-4-hydroxybenzonitrile 20 g
tri-(3,5,5-trimethylhexyl)amine 22.9 g
cyclohexanone
q.s. to give 100 cc. of solution 70

- (vii) Tributylamine salt of 3,5-diiodo-4-hydroxybenzonitrile from

- 3,5-diiodo-4-hydroxybenzonitrile 20 g
tributylamine 9.97 g
cyclohexanone
q.s. to give 100 cc of solution. 75

- (viii) Tributylamine salt of 3,5-dibromo-4-hydroxybenzonitrile from 80

- 3,5-dibromo-4-hydroxybenzonitrile 20 g
tributylamine 13.36 g
cyclohexanone
q.s. to give 100 cc of solution. 85

EXAMPLE XIII.

A solution of calcium chloride hexahydrate (22 g.) in water (150 cc.) is added, with stirring, to a solution of the sodium salt of 3,5-diiodo-4-hydroxybenzonitrile (52.5 g; assay as sodium salt 80%) in water (500 cc.). The white product which separates is collected, washed with a small quantity of water (25 cc.) and dried at 120° C, giving the calcium salt of 3,5-diiodo-4-hydroxybenzonitrile (33 g.) 90 95

EXAMPLE XIV.

A saturated solution of ammonia in ethanol (20 cc.) is added to a suspension of 3,5-dibromo-4-hydroxybenzonitrile (13.8 g.) in ethanol (25 cc.) and the mixture allowed to stand overnight in a closed vessel. The white product is then collected, washed successively with ethanol (10 cc.), tetrahydrofuran (10 cc.) and diethyl ether (10 cc.) and dried in air at room temperature (ca. 20° C.), giving the 100 105

ammonium salt of 3,5-dibromo-4-hydroxybenzonitrile (12.5 g.)

The ammonium salt of 3,5-diiodo-4-hydroxybenzonitrile is similarly obtained as a white solid.

EXAMPLE XV.

An ethanolic solution of monomethylamine (33%; 20cc.) is added to a suspension of 3,5-diiodo-4-hydroxybenzonitrile (18.5 g.) in ethanol (25 cc.) and the mixture allowed to stand overnight in a closed vessel. The white product is collected, washed successively with ethanol (15 cc.) tetrahydrofuran (15 cc.) and diethylether (15 cc.) and dried in air at room temperature (ca. 20° C.) giving the monomethylamine salt of 3,5-diiodo-4-hydroxybenzonitrile (17.5 g.).

The dimethylamine salt is similarly prepared in the form of a white solid using a 33% ethanolic solution of dimethylamine.

EXAMPLE XVI.

An ethanolic solution of trimethylamine (33%; 20 cc.) is added to a suspension of 3,5 - diiodo - 4 - hydroxybenzonitrile (18g.) in ethanol (25 cc.) and the mixture allowed to stand overnight in a closed vessel. The white product is collected, washed with ethanol (15cc.) followed by diethylether (20 cc.) and dried in air, giving the trimethylamine salt of 3,5-diiodo-4-hydroxybenzonitrile (17g.).

The monomethylamine salt of 3,5-dibromo-4-hydroxybenzonitrile is similarly prepared in the form of a white solid using a 33% ethanolic solution of monomethylamine.

EXAMPLE XVII.

An ethanolic solution of dimethylamine (33%; 15 cc.) is added to a suspension of 3,5 - dibromo - 4 - hydroxybenzonitrile (13.8g) in ethanol (25 cc.) and the mixture allowed to stand overnight in a closed vessel. The white product is collected, successively washed with ethanol (10 cc.) tetrahydrofuran (10 cc.) and diethylether (10 cc.) and dried in air at room temperature (ca. 20° C.) giving the dimethylamine salt of 3,5-dibromo-4-hydroxybenzonitrile (14.5 g.).

EXAMPLE XVIII.

3,5 - Dibromo - 4 - hydroxybenzonitrile (13.8 g.) is dissolved in an ethanolic solution of trimethylamine (33%; 15cc.). After standing overnight in an open dish at room temperature (ca. 20° C.) the semi-solid residue is triturated with diethyl ether (25 cc.) and dried in air at 20° C., giving the trimethylamine salt of 3,5-dibromo-4-hydroxybenzonitrile (8 g.) as a white solid.

EXAMPLE XIX.

3,5 - Dibromo - 4 - hydroxybenzonitrile (55.4 g.) and diethanolamine (21 g.) are dissolved in dry methanol (500 cc.). The methanol is allowed to evaporate spontaneously in an

open dish and the sticky residue dried *in vacuo* over silica gel, giving the diethanolamine salt of 3,5 - dibromo - 4 - hydroxybenzonitrile (76 g.) as a free flowing white solid.

The mono- and triethanolamine salts of 3,5 - dibromo - 4 - hydroxybenzonitrile and the mono-, di- and triethanolamine salts of 3,5 - diiodo - 4 - hydroxybenzonitrile can be prepared similarly.

The following procedures 1, 2 and 3 illustrate the preparation of 3,5-diiodo-4-hydroxybenzonitrile:—

PROCEDURE 1

Concentrated sulphuric acid (22.7 cc) is added to a mixture of 4-acetoxybenzonitrile (21.9 g) and ethanol (158 cc) with cooling so that the temperature does not exceed 55° C. A solution of potassium iodide (37.8 g) and potassium iodate (24.5 g) in water (450 cc) is added at 55° C to the stirred mixture. After an initial exothermic reaction (which is controlled by external cooling), the temperature falls to 45° C. The mixture is maintained at 50° C. for 2 hours and, after standing overnight at ambient temperature (15—25° C.), sufficient sodium metabisulphite is added to destroy excess iodine present. The product is filtered off and dried at 40° C. to give 3,5-diiodo - 4 - hydroxybenzonitrile (48.5 g), m.p. 205° C. (melting point not depressed by admixture with an authentic sample of 3,5-diiodo - 4 - hydroxy - benzonitrile, m.p. 206—208° C. but depressed by admixture with an authentic sample of 3,5-diiodo-4-acetoxybenzonitrile, m.p. 204—207° C.).

PROCEDURE 2

4-hydroxybenzonitrile (1.62 kg) is stirred with a solution of potassium hydroxide (777 g) in water (15 litres) until solution is complete. Potassium iodide (3.38 kg), potassium iodate (2.445 kg) and water (45 litres) are then successively added and stirring continued until solution is complete. The solution is stirred with charcoal (25 g), filtered, and the filtrate added, over 1 hour, to a stirred mixture of ethanol (15.84 litres) and concentrated sulphuric acid (2.643 litres) at 55° C. During the addition, the temperature of the mixture slowly falls to 50° C. The mixture is then stirred and heated (in a steam jacket) under reflux for 2 hours, cooled to 15° C. and stirred with sodium metabisulphite (500 g) to remove excess iodine. The solid product is then filtered off, washed with water (3×3.6 litres) and dried at 60° C., giving 3,5-diiodo-4-hydroxybenzonitrile (4.86 kg), m.p. 208—211° C.

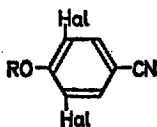
PROCEDURE 3

A solution of 4-hydroxybenzonitrile (22 g) in glacial acetic acid (75 cc) was warmed to 95° C. on a water bath and heating discontinued while freshly prepared iodine mono-

chloride (68 g) in glacial acetic acid (50 cc) was added as rapidly as possible. On completion of the addition, heating was continued and boiling water (100 cc portions) added after 15, 30 and 60 minutes. Five minutes after the last addition of boiling water, the mixture was allowed to cool. The solid product was collected by filtration and, in order to remove excess iodine, washed with sodium metabisulphite (10 g dissolved in water (50 cc)) and four times with water (50 cc). Drying in an oven at 80° C. gives 3,5-diiodo-4-hydroxybenzonitrile (54 g), m.p. 196—199° C.

15 WHAT WE CLAIM IS:—

1. A herbicidal composition suitable for agricultural use comprising at least one benzonitrile derivative which is a compound of the general formula:



I

wherein Hal represents a halogen atom, the two halogen atoms being identical; and R represents a hydrogen atom or an acetyl group or an alkali metal, ammonium or amine salt of a compound of general formula I in which R represents a hydrogen atom; in association with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions; with the proviso that when the benzonitrile derivative is a compound of formula I in which

(a) Hal represents a chlorine, bromine or iodine atom and R is a hydrogen or acetyl group, and the diluent is a liquid other than an animal oil, a mineral oil (as hereinbefore defined) or a vegetable oil, or

(b) Hal represents a chlorine, bromine or iodine atom, R is a sodium ion and the diluent is ethanol or aqueous ethanol, the diluent must be associated with a surface-active agent, an adhesive or another herbicidally active compound.

2. A herbicidal composition according to claim 1 wherein the benzonitrile derivative is homogeneously dispersed in the diluent or surface-active agent.

3. A herbicidal composition according to claim 1 or 2 wherein the diluent is a liquid which is other than animal oil, a vegetable oil or a mineral oil (as herein defined) and is associated with a surface-active agent, an adhesive or another herbicidally active compound; or is a solid; or is an animal oil, a mineral oil (as herein defined) or a vegetable oil.

4. A herbicidal composition according to any one of the preceding claims in which

the benzonitrile derivative is associated with a surface-active agent.

5. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a phenoxyalkanoic herbicide.

6. A herbicidal composition according to claim 5 in which the phenoxyalkanoic herbicide is MCPB, 2,4-DB, MCPA, 2,4-D, CMPP or 2,4-DP.

7. A herbicidal composition according to any one of the preceding claims in the form of a concentrate which requires dilution before use as a herbicide.

8. A herbicidal composition according to claim 7 in the form of a wettable powder.

9. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is water.

10. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is an organic liquid miscible with water.

11. A herbicidal composition according to any one of claims 1 to 7, 9 or 10 wherein the diluent is a solvent for the benzonitrile derivative.

12. A herbicidal composition according to claim 11 in the form of a concentrate which is emulsifiable in water.

13. A herbicidal composition according to any one of the preceding claims wherein Hal represents an iodine atom.

14. A herbicidal composition according to any one of claims 1 to 12 wherein Hal represents a bromine atom.

15. A herbicidal composition according to any one of claims 1 to 12 wherein Hal represents a chlorine atom.

16. A herbicidal composition according to any one of claims 1 to 12 wherein the benzonitrile derivative is 3,5-diiodo-4-hydroxybenzonitrile or an alkali metal salt thereof, 3,5-dibromo-4-hydroxybenzonitrile or an alkali metal salt thereof, 3,5-diiodo-4-acetoxybenzonitrile or 3,5-dibromo-4-acetoxybenzonitrile.

17. A herbicidal composition according to any one of claims 1 to 12 wherein the benzonitrile derivative is 3,5-dichloro-4-hydroxybenzonitrile or a salt thereof, or 3,5-dichloro-4-acetoxybenzonitrile.

18. A herbicidal composition according to claim 1, wherein the benzonitrile derivative is an alkali metal salt of 3,5-diiodo-4-hydroxybenzonitrile or 3,5-dibromo-4-hydroxybenzonitrile and is associated with a compatible diluent.

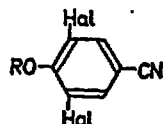
19. A herbicidal composition according to claim 1, wherein the benzonitrile derivative is 3,5-dibromo-4-hydroxybenzonitrile or 3,5-diiodo-4-hydroxybenzonitrile and is associated with a compatible diluent.

20. A herbicidal composition according to any one of claims 1 to 12, wherein the benzonitrile derivative is an amine or ammonium

chloride (68 g) in glacial acetic acid (50 cc) was added as rapidly as possible. On completion of the addition, heating was continued and boiling water (100 cc portions) added after 15, 30 and 60 minutes. Five minutes after the last addition of boiling water, the mixture was allowed to cool. The solid product was collected by filtration and, in order to remove excess iodine, washed with sodium metabisulphite (10 g dissolved in water (50 cc)) and four times with water (50 cc). Drying in an oven at 80° C. gives 3,5-diiodo-4-hydroxybenzonitrile (54 g), m.p. 196—199° C.

15 WHAT WE CLAIM IS:—

1. A herbicidal composition suitable for agricultural use comprising at least one benzonitrile derivative which is a compound of the general formula:



I

wherein Hal represents a halogen atom, the two halogen atoms being identical; and R represents a hydrogen atom or an acetyl group or an alkali metal, ammonium or amine salt of a compound of general formula I in which R represents a hydrogen atom; in association with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions; with the proviso that when the benzonitrile derivative is a compound of formula I in which

(a) Hal represents a chlorine, bromine or iodine atom and R is a hydrogen or acetyl group, and the diluent is a liquid other than an animal oil, a mineral oil (as hereinbefore defined) or a vegetable oil, or

(b) Hal represents a chlorine, bromine or iodine atom, R is a sodium ion and the diluent is ethanol or aqueous ethanol, the diluent must be associated with a surface-active agent, an adhesive or another herbicidally active compound.

2. A herbicidal composition according to claim 1 wherein the benzonitrile derivative is homogeneously dispersed in the diluent or surface-active agent.

3. A herbicidal composition according to claim 1 or 2 wherein the diluent is a liquid which is other than animal oil, a vegetable oil or a mineral oil (as herein defined) and is associated with a surface-active agent, an adhesive or another herbicidally active compound; or is a solid; or is an animal oil, a mineral oil (as herein defined) or a vegetable oil.

4. A herbicidal composition according to any one of the preceding claims in which

the benzonitrile derivative is associated with a surface-active agent.

5. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a phenoxyalkanoic herbicide.

6. A herbicidal composition according to claim 5 in which the phenoxyalkanoic herbicide is MCPB, 2,4-DB, MCPA, 2,4-D, CMPP or 2,4-DP.

7. A herbicidal composition according to any one of the preceding claims in the form of a concentrate which requires dilution before use as a herbicide.

8. A herbicidal composition according to claim 7 in the form of a wettable powder.

9. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is water.

10. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is an organic liquid miscible with water.

11. A herbicidal composition according to any one of claims 1 to 7, 9 or 10 wherein the diluent is a solvent for the benzonitrile derivative.

12. A herbicidal composition according to claim 11 in the form of a concentrate which is emulsifiable in water.

13. A herbicidal composition according to any one of the preceding claims wherein Hal represents an iodine atom.

14. A herbicidal composition according to any one of claims 1 to 12 wherein Hal represents a bromine atom.

15. A herbicidal composition according to any one of claims 1 to 12 wherein Hal represents a chlorine atom.

16. A herbicidal composition according to any one of claims 1 to 12 wherein the benzonitrile derivative is 3,5-diiodo-4-hydroxybenzonitrile or an alkali metal salt thereof, 3,5-dibromo-4-hydroxybenzonitrile or an alkali metal salt thereof, 3,5-diiodo-4-acetoxymbenzonitrile or 3,5-dibromo-4-acetoxymbenzonitrile.

17. A herbicidal composition according to any one of claims 1 to 12 wherein the benzonitrile derivative is 3,5-dichloro-4-hydroxybenzonitrile or a salt thereof, or 3,5-dichloro-4-acetoxymbenzonitrile.

18. A herbicidal composition according to claim 1, wherein the benzonitrile derivative is an alkali metal salt of 3,5-diiodo-4-hydroxybenzonitrile or 3,5-dibromo-4-hydroxybenzonitrile and is associated with a compatible diluent.

19. A herbicidal composition according to claim 1, wherein the benzonitrile derivative is 3,5-dibromo-4-hydroxybenzonitrile or 3,5-diiodo-4-hydroxybenzonitrile and is associated with a compatible diluent.

20. A herbicidal composition according to any one of claims 1 to 12, wherein the benzonitrile derivative is an amine or ammonium





salt of 3,5-diiodo- or 3,5-dibromo-4-hydroxybenzonitrile.

21. A herbicidal composition comprising at least one benzonitrile derivative which is an alkaline earth metal salt of a compound of general formula I as defined in claim 1 in which R represents a hydrogen atom, in association with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions.

22. A herbicidal composition according to claim 21 wherein the benzonitrile derivative is homogeneously dispersed in the diluent or surface-active agent.

23. A herbicidal composition according to claim 21 or 22 wherein the diluent is a liquid which is other than an animal, vegetable or mineral oil (as hereinbefore defined) and contains a surface active agent; or a solid; or an animal, vegetable or mineral oil (as hereinbefore defined).

24. A herbicidal composition according to claim 21 or 22 wherein the benzonitrile derivative is associated with a diluent and a surface-active agent.

25. A herbicidal composition according to any one of claims 21 to 24, wherein the benzonitrile is associated with a phenoxyalkanoic herbicide.

26. A herbicidal composition according to claim 25, wherein the phenoxyalkanoic herbicide is MCPB, 2,4-DB, MCPA, 2,4-D, CMPP or 2,4-DP.

27. A herbicidal composition according to any one of claims 21 to 26 in the form of a concentrate which requires dilution before use as a herbicide.

28. A herbicidal composition according to any one of claims 21 to 27 wherein the diluent is as defined in claim 8, 9, 10 or 11.

29. A herbicidal composition according to any one of claims 21 to 28 wherein Hal is as defined in any one of claims 13 to 15.

30. A herbicidal composition according to any one of claims 21 to 28 wherein the benzonitrile derivative is a calcium salt of 3,5-diiodo- or 3,5-dibromo-4-hydroxybenzonitrile.

31. A herbicidal composition according to claim 1 or 21 substantially as described.

32. As new compounds, benzonitrile derivatives which are alkaline earth metal salts of compounds of general formula I as defined in claim 1 wherein R is a hydrogen atom.

33. As new compounds, the calcium salts of 3,5-diiodo-4-hydroxybenzonitrile and 3,5-dibromo-4-hydroxybenzonitrile.

34. As new compounds, benzonitrile derivatives which are compounds of general formula I as defined in claim 1 and alkali metal, ammonium and amine salts of such compounds in which R represents hydrogen, with the proviso that when Hal represents a chlorine, bromine or iodine atom, R does not represent a hydrogen atom, a sodium ion or an acetyl

group and with the further proviso that when Hal represents an iodine atom R does not represent a potassium ion.

35. As new compounds, the amine salts of compounds of general formula I as defined in claim 1 wherein the amine comprises one or more organic groups containing at least 4 carbon atoms.

36. As new compounds, the ammonium salts of 3,5-diiodo-4-hydroxybenzonitrile and 3,5-dibromo-4-hydroxybenzonitrile.

37. As a new compound, the potassium salt of 3,5-dibromo-4-hydroxybenzonitrile.

38. A method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicide in the form of at least one benzonitrile derivative which is a compound of general formula I as defined in claim 1 or an alkali metal, alkaline earth metal, ammonium or amine salt of such a compound in which R represents a hydrogen atom.

39. A method according to claim 38 wherein there are weeds visible at the locus at the time when the benzonitrile derivative is applied.

40. A method according to claim 38 or 39 wherein the weeds whose growth is controlled are broad-leaved weeds.

41. A method according to any one of claims 38 to 40 wherein the benzonitrile derivative is applied to a crop-growing area (as hereinbefore defined), containing broad-leaved weeds sensitive to said derivative, at a rate sufficient to control the growth of weeds without causing substantial permanent damage to the crop.

42. A method according to claim 41 wherein the benzonitrile derivative is applied to a growing crop.

43. A method according to claim 41 or 42 wherein the crop is graminaceous.

44. A method according to claim 41 wherein the crop is a cereal or a grass.

45. A method according to claim 41 or 42 wherein the crop is a legume.

46. A method according to claim 41 or 42 wherein the crop is flax, linseed, carrots, onions, or a cruciferous crop.

47. A method according to any one of claims 41 to 45 wherein the benzonitrile derivative is applied at a rate of up to 0.56 kg. per hectare.

48. A method according to claim 43 or 44 wherein the benzonitrile derivative is applied at a rate of up to 1.68 kg. per hectare.

49. A method according to claim 41 wherein the benzonitrile derivative is applied to an area on which crops are growing, in a directional manner which results in the benzonitrile derivative being applied preferentially against the weeds rather than against the crop.

50. A method according to claim 49 wherein the crop-growing area is a plantation, orchard or vineyard.

51. A method according to any one of



claims 38 to 40 wherein the benzonitrile derivative is applied to fallow or uncultivated land.

5 52. A method according to any one of claims 49 to 51 wherein the benzonitrile derivative is applied at a rate of 2.24 to 4.48 kg. per hectare.

10 53. A method of desiccating the foliage on crops such as potato, cotton, hops and leguminous seed crops which comprises applying to the crops at least one benzonitrile derivative as defined in claim 38.

54. A method according to claim 53 wherein the crop is potato or cotton.

15 55. A method according to claim 53 or 54 wherein the benzonitrile derivative is applied at a rate of 1.12 to 4.48 kg. per hectare.

20 56. A method according to any one of claims 38 to 55 wherein the benzonitrile derivative is a compound of general formula I as defined in claim 1 or an alkali metal, ammonium or amine salt of such a compound in which R is a hydrogen atom.

25 57. A method according to claim 56 wherein Hal represents an iodine, bromine or chlorine atom.

30 58. A method according to claim 56 wherein the benzonitrile derivative is 3,5-diiodo-4-hydroxybenzonitrile or an alkali metal salt thereof.

35 59. A method according to claim 56 wherein the benzonitrile derivative is 3,5-dibromo-4-hydroxybenzonitrile or an alkali metal salt thereof.

40 60. A method according to claim 56 wherein the benzonitrile derivative is 3,5-diiodo-4-acetoxybenzonitrile or 3,5-dibromo-4-acetoxybenzonitrile.

61. A method according to any one of claims 56 to 60 wherein the benzonitrile derivative is associated with a liquid diluent other than an animal, vegetable or mineral oil (as herein defined).

62. A method according to claim 61 wherein the benzonitrile derivative is homogeneously dispersed in the diluent. 45

63. A method according to any one of claims 38 to 55 which comprises applying a herbicidal composition as claimed in any one of claims 1 to 31. 50

64. A method according to any one of claims 38 to 44, 51, 52 and 54 which comprises applying a herbicidal composition as claimed in any one of claims 1 to 20. 55

65. A method according to any one of claims 38 to 44, 51, 52 and 54 which comprises applying a benzonitrile derivative as defined in any one of claims 56, 57 or 60. 60

66. A method according to any one of claims 38 to 44, 51, 52 and 54 which comprises applying a benzonitrile derivative as defined in claim 58 or 59. 65

67. A method according to claim 38 wherein the benzonitrile derivative is 3,5-dibromo-4-hydroxybenzonitrile or 3,5-diiodo-4-hydroxybenzonitrile. 70

68. A method according to claim 38 wherein the benzonitrile derivative is an alkali metal salt of 3,5-dibromo-4-hydroxybenzonitrile or 3,5-diiodo-4-hydroxybenzonitrile. 75

69. A method according to claim 68, wherein the benzonitrile derivative is applied to a crop-growing area containing broad-leaved weeds, said crop being a cereal crop.

70. A method of controlling the growth of weeds substantially as described.

71. A method of controlling the growth of weeds substantially as described in any one of the foregoing Examples.

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