

L194433



PATENT SPECIFICATION

L194433

NO DRAWINGS

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COMPLETE SPECIFICATION

Processes and Compositions for the Regulation of Plant Growth

We, AMCHEM PRODUCTS, INC., a Corporation organised under the Laws of the State of Delaware, United States of America, of Brookside Avenue, Ambler, Pennsylvania, 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 concerns processes and compositions for regulating the growth of plants.

We have found that certain derivatives of phosphonic acid exhibit marked powers to regulate the growth of plants. Many types of compounds have of course been proposed in the past for use as plant growth regulators, and some of these have found commercial application. As with other plant growth regulators, the phosphonic acid derivatives used according to this invention can produce the most diverse effects upon plants, dependent on a great many factors—including for instance the stage in the life-cycle of a plant at which they are applied to it, the concentration at which they are applied to the plant, and so on. The phosphonic acid derivatives of this invention when suitably used, as by anyone accustomed to the use of plant-growth regulators, can achieve the most marked and commercially-valuable effects, such as inducing and increasing flowering, suppression of apical dominance, auxin activity, increase in branching on certain plant species, increase in the protein content of certain plants, defoliation and fruit abscission effects, minimizing lodging in cereals, beans and peas, breaking dormancy in seeds, tubers and rhizomes, lending freeze resistance, ripening effects, and so on. Some

of these plant growth regulation effects have of course been achieved in the past by other means, but we have found that, over a wide range of plant species and conditions of application, the phosphonic acid derivatives used according to this invention yield results at least as good as and often superior to those attainable with conventional plant-growth regulators, with a marked ease of application as will be explained hereinafter.

The phosphonic acid derivatives of this invention are certain specific substituted phosphonic acids and their acid chlorides, anhydrides, hydrolyzable esters and salts—which for convenience we shall hereinafter collectively call “the phosphonic acid derivatives”. Derivatives of phosphonic acid chemically rather dissimilar to those used in the present invention have previously been suggested for use in agriculture as herbicides (see for instance U.S. Patent Specifications Nos. 2,927,014 and 3,223,514) but the plant-growth regulating activity of the phosphonic acid derivatives of this invention is quite distinct from the herbicidal activity possessed by those known compounds. Although the phosphonic acid derivatives of this invention can sometimes be used in a herbicidal context (thus to stimulate the growth of dormant rhizomes in order to make them more susceptible to a herbicide) they are not themselves in any practical sense herbicides.

According to this invention there is provided a process for regulating plant growth, in which there is applied to the plant an effective amount of a plant growth regulator comprising one or more phosphonic acid derivatives conforming to the general formula

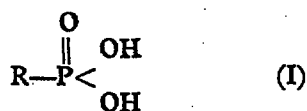
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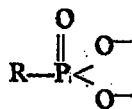
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where R is a vinyl, allyl, haloethyl, halopropyl, methoxyethyl, carboxymethyl or phosphonoethyl group, and/or the corresponding acid chlorides and/or anhydrides and/or amides and/or hydrolyzable mono- and di-esters and/or salts thereof.

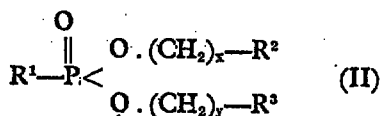
So far as we can determine, the plant-growth regulating activity of the phosphonic acid derivatives defined with reference to formula I resides in the



anion, (presuming the acid chloride and anhydride hydrolyze to form it) and we believe that any derivative of that anion capable of releasing it in, on or around the plant under treatment will display the desired plant-growth regulating activities. Now obviously, the possible derivatives include both compounds which hydrolyse very readily as well as also compounds which hydrolyse only with difficulty, perhaps owing to steric hindrance. Moreover, there are compounds which in the laboratory can be hydrolysed only with difficulty, yet which apparently can be metabolized by the plant and hydrolysed by its enzymatic systems quite readily.

In general we therefore recommend that the phosphonic acid derivatives employed should normally be compounds known to be readily hydrolysable, either in the laboratory or the plant under treatment. If for any reason the use of other derivatives is contemplated, it will then be necessary to investigate whether on a particular plant under particular conditions that derivative is capable of yielding the desired results. If not, the choice of compound must be adjusted accordingly, moving towards a more readily hydrolysed derivative. Initial guidance in the choice of any particular phosphonic acid derivative can be secured in the greenhouse by testing its power produce epinasty in tomato plants, using the routine standard methods.

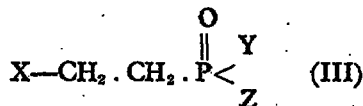
The investigation suggested above is well within the competence of any plant biologist. For assistance, however, it may be noted that the majority (though not all) of the phosphonic acid derivatives which we recommend are the phosphonic acid derivatives conforming to the general formula



in which one of x and y is 0 and the other is 0 or 1; R¹ (like R in formula I above) is a vinyl, allyl, haloethyl, halopropyl, methoxyethyl, carboxymethyl or phosphonoethyl group; R² is a hydrogen atom or a substituted or unsubstituted phenyl group; and R³ is a hydrogen atom or a substituted or unsubstituted phenyl group or a halogen-substituted or unsubstituted, saturated or unsaturated hydrocarbon chain containing from 2 to 12 carbon atoms.

Furthermore, we have also found that in general the phosphonic acid derivatives which display the most consistently satisfactory results as plant-growth regulators are those in which R/R¹ in general formulae I/II above is a substituted-ethyl group, and indeed more particularly either a phosphono-substituted ethyl group (this phosphono-substituent may be further substituted in the same way as the phosphono-grouping at the other end of the ethyl group) or above all a halogen-substituted ethyl group.

Thus, the particularly preferred phosphonic acid derivatives for use according to the present invention are the (halo/phosphono)-ethyl phosphonic acid derivatives conforming to the general formula



where X is a halogen atom or a phosphono-PO(Y)Z group; Y is a chlorine atom or an -OR⁴ group; R⁴ is an hydrogen atom or a salt-forming cation or a substituted or unsubstituted aryl-, arylmethylene-, heterocyclyl- or heterocyclylmethylene group, or the X·CH₂·CH₂·PO(Z)- group; and Z is defined as (but not necessarily identical to) Y or is an oxyhydrocarbon group, wherein the hydrocarbon chain may be substituted or unsubstituted, saturated or unsaturated; or Z and R⁴ together form an -O-Ø-, -O·CH₂-Ø-, -CO·O-Ø- or -CO·NH-Ø- linkage, where Ø represents a divalent, substituted or unsubstituted benzene or heterocyclic ring.

In general formula III above, it is to be understood that the term "aryl" refers especially to monocyclic aryl groups, whether substituted or not, but may extend also to bicyclic and polycyclic aryl groups provided that they bear one or more substituents capable of imparting water-solubility to the compound as a whole, such as sulphonate groups.

In both general formulae II and III above, the substituted or unsubstituted, saturated or unsaturated hydrocarbon chains will normally be lower alkyl or cyclo-alkyl groups, such as ethyl, isopropyl, butyl and cyclohexyl groups. We recommend that the hydrocarbon grouping should contain from 2 to 18 carbon atoms,

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since above 18 carbon atoms we have found that the water-solubility of the compound as a whole decreases undesirably.

- 5 The salt-forming cations may be chosen from the wide variety already used in agricultural chemicals, and for instance include sodium, aluminium and zinc. However, for reasons of stability which will become apparent hereinafter we normally prefer to avoid the use of readily-hydrolysable salts.

- 10 For reasons of cost and effectiveness we much prefer to employ 2-chloroethyl phosphonic acid and its derivatives, notably the anhydride of 2-chloroethyl phosphonic acid, the bis-(acid chloride) of 2-chloroethyl-phosphonic acid, the pyrocatechol cyclic diester of 2-chloroethyl phosphonic acid, the 4-chloro-pyrocatechol cyclic diester of 2-chloroethyl phosphonic acid, the mixed ethyl and 2-hydroxyphenyl diester of 2-chloroethyl phosphonic acid, the mixed butyl and 2-hydroxyphenyl diester of 2-chloroethyl phosphonic acid, the mixed propynyl and 2-hydroxy-phenyl diester of 2-chloroethyl phosphonic acid, the bis-(pentachloro-phenyl) diester of 2-chloroethyl phosphonic acid, the 2-chloroethyl monoester of 2-chloroethyl phosphonic acid, the bis-(phenyl) diester of 2-chloroethyl phosphonic acid, the tetrachloro-pyrocatechol cyclic ester of 2-chloroethyl phosphonic acid, the saligen cyclic ester of 2-chloroethyl phosphonic acid, the salicylic acid cyclic ester of 2-chloroethyl phosphonic acid, the 3-hydroxy-phenyl-monoester of 2-chloroethyl phosphonic acid (in polymeric form), the bis-(2-oxo-pyrrolidinyl-methyl) diester of 2-chloroethyl phosphonic acid, the mixed phenyl and *o*-hydroxy-phenyl diester of 2-chloroethyl phosphonic acid, the *o*-hydroxy-phenyl monoester of 2-chloroethyl phosphonic acid, the mixed isopropyl and 2-hydroxy-phenyl diester of 2-chloroethyl phosphonic acid, the mixed octyl and 2-hydroxy-phenyl diester of 2-chloroethyl phosphonic acid, the salicylic acid cyclic ester of 2-chloroethyl phosphonamidic acid, the mixed hexadecyl and 2-hydroxy-phenyl diester of 2-chloroethyl phosphonic acid, the mixed tridecyl and 2-hydroxyphenyl ester of 2-chloroethyl phosphonic acid, the 2,3-pyridine-diol cyclic ester of 2-chloroethyl phosphonic acid, and the bis-(2-chloroethyl)-diester of 2-chloroethyl phosphonic acid.

- 55 Broadly-speaking equally effective (subject naturally to adjustment of the application rate), though usually less desirable, are the corresponding 2-bromoethyl phosphonic acid and its derivatives, 2-iodo-ethyl phosphonic acid and its derivatives, and 2-fluoro-ethyl phosphonic acid and its derivatives, as well as the phosphono-ethyl phosphonic acid and its derivatives.

- 60 Besides the preferred phosphonic acid derivatives of general formula III listed above a number of other phosphonic acid derivatives

within general formulae I and II above which have been shown to be effective are as follows:—

Allyl phosphonic acid, vinyl phosphonic acid, 2,3-dichloro-propyl phosphonic acid, 2-methoxy-ethyl phosphonic acid, carboxymethyl phosphonic acid and 2-chloro-propyl phosphonic acid, as well as their corresponding derivatives such as for instance the pyrocatechol cyclic ester of vinyl phosphonic acid and the like.

It will be well understood by any plant biologist that, as with any plant-growth regulator, the phosphonic acid derivatives should be applied to any particular plant at certain optimum application rates (either of concentration in solution, or of weight per unit of ground area) and at certain stages in the growth cycle of the plant, if they are to achieve any particular desired growth regulating effect. While we have made very extensive investigations into the growth regulating properties of the phosphonic acid derivatives, the almost limitless variety of plant species and the great diversity of desirable plant responses, coupled also with the fairly wide range of climatic conditions which may be encountered, make it altogether impossible here to specify exact application rates for all purposes. Such application rates can however be determined fairly readily for any particular case by standard procedures well known in themselves. For general guidance, our experience indicates that when applied broadcast to standing vegetation, the application rate for the plant growth regulators of the invention will normally lie within the range of from 0.1 to 25—30 pounds per acre (or 0.112 to 27.5—33.6 kilos per hectare), usually in fact within the narrower range from 0.25 to 16 pounds per acre (or 0.28 to 17.92 kilos per hectare), and most frequently within the still narrower range of from 0.5 to 4 pounds per acre (or 0.56 to 4.48 kilos per hectare). When applied by drenching trees or soaking seeds or tubers the application rate for the plant growth regulators will normally lie within the range of from 1 to 48,000 parts per million (thus from 0.0001% to 4.8% by weight), and most often within the range of 10 to 10,000 parts per million (thus from 0.001% to 1% by weight). Further detailed guidance in relation to a variety of commercially-important agricultural usages will be found hereinafter.

The phosphonic acid derivatives when appropriately applied to plants within the limits suggested above have been found to cause a wide variety of plant growth responses, including for instance the following:—

Increasing Yields:

The phosphonic acid derivatives are capable of increasing yields of small grains, particularly oats (*Avena sativa*), wheat (*Triticum aestivum*), and barley (*Hordeum* spp.); and of

increasing yields of various types of beans and of cotton (*Gossypium hirsutum*);

Auxin Activity:

- When applied for instance as a lanolin paste, to one side of a decapitated sunflower hypocotyl the phosphonic acid derivatives are capable of inducing bending of the hypocotyl away from the side of the application; they are also capable of inducing sprouting of underground rhizomes of monocotyledonous and dicotyledonous plants; of causing cell proliferation; and of inducing rooting, as evidence by the production of large numbers of root primordia over the entire stem length of tomato plants (*Lycopersicon esculentum*) after these have been sprayed with an aqueous solution thereof—this type of response makes it possible to root cuttings either when taken from treated plants or after treatment of their cut ends.

Inhibition of Terminal Growth Control of Apical Dominance, Increase in Branching, and Increase in Tillering:

- These types of plant growth response can be produced on a variety of plant species when they are treated with the phosphonic acid derivatives including privet (*Ligustrum ovalifolium*), blueberry, (*Vaccinium corymbosum*), azalea (*Rhododendron obtusum*), soybeans (*Glycine max.*), snapbeans (*Phaseolus vulgaris*), tomatoes (*Lycopersicon esculentum*), alligator weed (*Alternanthera philoxeroides*) and monocotyledons such as rice (*Oryza sativa*), johnsongrass (*Sorghum halopense*) and wild oats (*Avena fatua*). This type of response can also be of value in the control of roadside grasses. It has been suggested that the removal of the lead bud (e.g. by pinching) should allow growth of auxiliary buds; but it is generally found that on removal of the lead bud one of the auxiliary buds takes over the activity and dominance of the lead bud. The use of the phosphonic acid derivatives, however, usually retards the activity of the lead bud for a while but then later restores the lead bud to normal growth, with production of normal flowers and normal fruit; and thus one avoids the permanent loss of buds inevitably associated with pinching. However, some plant species respond differently when treated with the phosphonic acid derivatives for control of apical dominance—growth inhibition may extend to include not only the lead but but also lateral buds along the stem. Examples of such plants are tobacco (*Nicotiana tabacum*) and chrysanthemum (*Chrysanthemum* sp.)—this type of response is useful for preventing sucker growth from lateral buds on tobacco.

Increasing Protein Content:

- The phosphonic acid derivatives are capable of measurably increasing the leaf area relative to the stem area in many plants, and the increased ratio of leaves to stem results in an increase in total protein on a per plant basis, and modification of the protein, carbo-

hydrate, fat, nicotine and sugar within the treated plant.

Abscission of Foliage, Flowers and Fruit:

The phosphonic acid derivatives have been found to accelerate abscission of mature foliage on both perennial and annual plant species. They are for instance quite active as defoliants on cotton, and defoliation properties have also been observed in other plant species such as roses, privet, apples, citrus, and brussel sprouts once the leaves have attained a mature state. Abscission of flowers and/or fruit following application of the phosphonic acid derivatives has been observed on a variety of plant species, including apples (*Malus domestica*), pears (*Pyrus communis*), cherries (*Prunus avium*), pecans (*Carya illinoensis*), grapes (*Vitis vinifera*), olives (*Olea europaea*), coffee (*Doffea arabica*) and snapbeans (*Phaseolus vulgaris*)—these abscission responses can be used to regulate flower production and as an aid in harvesting fruit.

Hastening Ripening and Colour Promotion in Fruit:

The phosphonic acid derivatives have been shown to be capable of hastening the ripening of fruit from a number of plant species, such as apples (*Malus domestica*), pears (*Pyrus communis*), cherries (*Prunus avium*), bananas, and pineapples (*Ananas comosus*); and of removing the green colour from harvestable fruit such as tomatoes (*Lycopersicon esculentum*) and regreened citrus such as oranges (*Citrus sinensis*) and lemons (*Citrus limon*).

Increasing Flowering and Fruiting:

Suitably applied, the phosphonic acid derivatives are capable of increasing flowering and fruiting in a number of economic crops, such as soybeans (*Glycine max.*), snapbeans (*Phaseolus vulgaris*), kidney beans (*Phaseolus vulgaris*) and zinnias (*Zinnia elegans*).

Abortion or Inhibition of Flowering and Seed Development:

Suitably applied, the phosphonic acid derivatives will inhibit flowering and/or abort seed development, for example in johnson grass (*Sorghum halepense*).

Prevention of Lodging:

Application of the phosphonic acid derivatives has been shown to induce rigor resulting in firmer and stronger plants capable of resisting natural tendencies towards lodging. This effect has been observed on a number of plant species, such as for example wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), and pea (*Pisum sativum*).

Stimulation of Seed Germination and Breaking of Dormancy:

The phosphonic acid derivatives have been shown to stimulate the germination of for instance lettuce seed and to terminate the dormancy of tubers such as seed potatoes.

Resistance to Freeze Injury:

The phosphonic acid derivatives appear to increase the hardiness of various plant species,

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such as for example, lima beans (*Phaseolus vulgaris*).

Hormone or Epinasty Effects:

5 The phosphonic acid derivatives have been shown to produce hormone or epinasty effects upon various plants, including notably tomatoes (*Lycopersicon esculentum*).

Interactions with other Growth Regulators:

10 The phosphonic acid derivatives may of course be used in conjunction with other plant growth regulators, such as, maleic hydroxide, N - dimethyl - aminosuccinic acid, gibberellic acid and naphthalene acetic acid, and interact therewith producing synergistic or antagonistic responses in various plants.

Interactions with Herbicides:

15 While the phosphonic acid derivatives seem to have essentially no phyto-toxic activity of their own, they may be used in their capacity as plant growth regulators in conjunction with herbicides, for instance with aminotriazole in the herbicidal control of johnson grass (*Sorghum halepense*).

25 The various types of plant growth response described above have in general been observed before; and at least many of them can also be caused by ethylene, which apparently plays a role in the growth cycle of plants. The role of ethylene in plant growth cycles has been discussed *inter alia* in "Plant Biochemistry", by James Bonner and J. E. Varner, (1965) pages 641—664. It is moreover known to employ ethylene, essentially in gaseous form, to stimulate flower initiation in pineapples—see for instance "Hormonal Control of Plant Growth", by N. S. Parihar, (1964) pages 69—79. Ethylene is applied upon a commercial scale using cumbersome equipment to drench the pineapple plants with ethylene-saturated liquids. It is also existing commercial practice to ripen bananas in an atmosphere containing ethylene. It has moreover been reported that essentially similar if less powerful effects on plant tissues are caused by other unsaturated hydrocarbon gases. The mechanism by which ethylene and the other gases affect the growth cycle of plants is far from fully understood, but it is clear that they do play a role. It can be seen that the phosphonic acid derivatives used according to the present invention contain in their structures molecular configurations potentially capable of breakdown into ethylene or like compounds. Some indeed of the phosphonic acid derivatives will slowly but spontaneously break-down hydrolytically to yield ethylene.

55 For these reasons, while we do not wish to be limited by any theoretical considerations, our belief is that the phosphonic acid derivatives used according to the present invention probably in most cases exert their plant-growth regulating properties via the ethylene-responsive mechanism in plants.

60 It cannot be absolutely excluded that upon application of the phosphonic acid derivatives

in say aqueous solution they sometimes break-down outside the plant, while still in the aqueous solution in which they were applied, and the ethylene thus released is assimilated by the plant in gaseous form—but this seems very improbable, since even when stabilized against hydrolytic breakdown the phosphonic acid derivatives according to the invention will to a greater or lesser extent exert plant growth regulating activity when applied to plants, as demonstrated for instance by epinasty tests upon tomato plants.

70 It is therefore our belief that the phosphonic acid derivatives of this invention exert their growth regulating activity, at least in the great majority of cases, by assimilation into the metabolic system of the plant. Indeed, our analytical investigations have shown that, immediately following application to the plant, residues of these phosphonic acid derivatives are for a limited period to be found in the plant tissues. Our analytical investigations have also shown that in many plants some time after application of the phosphonic acid derivatives the plant tissues contain detectable amounts of ethylene. From this one might conclude that the phosphonic acid derivatives are broken-down within plant tissues to release ethylene, and that the ethylene thus released exerts its normal functions. It might therefore be supposed that this merely causes the artificial acceleration of the plants natural life cycle to another. Now, while it is true that such an acceleration does indeed happen, this is not the only effect observed. Thus not only does a plant growth regulating effect occur, but in most cases it occurs to a greater degree than in nature. Our analytical investigations have very surprisingly indicated that, with at least the preferred phosphonic acid derivatives on some plant species, the amount of ethylene present in the plant tissues is greater than that attributable to the phosphonic acid derivatives. Where we have detected this phenomenon, it seems that the quantity of ethylene released within the plant tissues is approximately twice that which can be derived from the quantity of phosphonic acid derivatives assimilated by those tissues. If this be so, it is clear that the assimilation of the phosphonic acid derivatives by the plant tissues may trigger-off the enzymatic or other systems within the plant which themselves generate ethylene.

100 The generally superior plant growth regulating activity of the haloethyl- and phosphonoethyl- phosphonic acid derivatives (of general formula III) used according to this invention could then be explained on the basis of this hypothesis, as follows. All the phosphonic acid derivatives of general formula I may be supposed to be capable of triggering the plant's internal enzymatic systems to a greater or lesser extent, to generate ethylene from the plant's own resources. The use of the preferred halo/phosphono-ethyl phosphonic acid deriva- 130

tives of general formula III however either increases the plant's own resources or merely results in break-down of the phosphonic acid derivatives to yield additional ethylene within the plant tissues.

As already indicated, despite the already very extensive research we have made into the mechanism whereby the phosphonic acid derivatives used according to the present invention exert their plant growth regulating properties, we are not yet able to say whether the theory advanced above concerning their mode of action is correct. At present however we believe this mode of action to be the most likely explanation of the plant growth regulating activity of these phosphonic acid derivatives.

In that belief, therefore, we regard our invention as providing a process for the regulation of plant growth in which there is applied to the plant an amount of one or more of the previously-specified phosphonic acid derivatives sufficient to trigger the ethylene-responsive mechanism in the plant.

It is a major advantage of the phosphonic acid derivatives used according to this invention, as compared with the generality of known plant growth regulators, that they tend to be cheaper, which reduces initial manufacturing cost, and they are nearly all water-soluble which reduces the cost of formulation and application.

Any derivatives which are not water-soluble can of course be dissolved in organic media or in aqueous media including organic co-solvents, or dispersed in aqueous media including surfactants and/or dispersing agents and/or emulsifying agents. The phosphonic acid derivatives may also be dispersed in or on pulverulent solid carriers such as vermiculite, attaclay, talc and the like.

The compositions based on liquid media will normally have a water-thin consistency, and can then be applied with any form of conventional agricultural spraying or like equipment. The compositions based on solid carriers may be applied in the form of powder or granules by the appropriate conventional distribution equipment. Although the preferred method of application is directly to the foliage and stems of the plants, the plant-growth regulating compositions containing the phosphonic acid derivatives are efficacious when applied to the soil in which the plants are growing, since apparently they can be root-absorbed to a sufficient extent to yield the desired plant responses.

While it is clear that in applying the phosphonic acid derivatives to standing crops and other vegetation the significant factor is the quantity of the plant growth regulating phosphonic acid derivative which is assimilated by the plants, we have already previously indicated the broad ranges of application rate per unit area of ground which in the majority

of cases should be recommended, and it may be added that the indicated amounts of the phosphonic acid derivatives may in general be applied in liquid formulations with sufficient aqueous or other liquid diluent so that the total volume sprayed is from about 1 to 100 U.S. gallons per acre (approximately 9.352 to 935.2 litres per hectare, hence roughly 10 to 1,000 litres per hectare; or approximately 0.832 to 83.2 British gallons per acre, hence very roughly 1 to 80 British gallons per acre).

From another aspect this invention also therefore broadly provides plant growth regulating compositions which contain one or more of the phosphonic acid derivatives previously defined herein together with a liquid solvent or dispersion medium or a pulverulent and/or granular solid carrier.

In the compositions ready for application to plants the amount of the phosphonic acid derivative(s) should usually be from 1 to 48,000 ppm., and preferably from 10 to 10,000 ppm.

In the aqueous liquid concentrates normally sold in commerce the concentration of the phosphonic acid derivative(s) may advantageously be in the range of from 10% to 30% (by weight).

The compositions may sometimes with advantage incorporate surfactants and/or dispersing agents and/or emulsifiers and/or penetrants and/or sequestrants and/or stabilizers. As previously indicated they may also sometimes for specific purposes incorporate other plant growth regulators and/or herbicides—though it is perhaps more realistic to envisage the phosphonic acid derivative(s) as additives for herbicidal compositions rather than the reverse. The compositions when aqueous may wherever necessary incorporate organic co-solvents to aid in solubilization of any water-insoluble compounds.

As regards stability, especially of the liquid concentrates as normally sold in commerce, it should be noted that few if any of the phosphonic acid derivatives are wholly stable upon prolonged storage in the presence of moisture, unless they are stabilized against break-down. Even the most stable of these phosphonic acid derivatives are liable ultimately to break-down, and the preferred (halo/phosphono)-ethyl phosphonic acid derivatives are on the whole especially troublesome in this respect. Since even non-aqueous compositions cannot wholly be protected from moisture it is very desirable that all the compositions should contain a stabilizer.

We have found that in general the phosphonic acid derivatives may most readily be stabilized against water or moisture by incorporating an acid therein to ensure that the pH is never greater than 5. The term "acid" in this context is used broadly to cover any material capable of imparting the desired pH value.

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The compositions can with advantage therefore incorporate a buffering agent to maintain the pH of the composition at the desired value of 5 or less.

Whether liquid or solid, the compositions cannot (except by extra-ordinary special precautions) be wholly freed from moisture, and even in the presence of acid/buffer systems as suggested above the possibility of hydrolytic break-down of the phosphonic acid derivatives with consequent release of ethylene cannot be excluded. This problem presents dangers, particularly with concentrates of the types normally solid in commerce, because the released ethylene can build up pressures within the container, which moreover is liable to be corroded by the acid composition, and ethylene is a flammable gas.

It is therefore a specific preferred feature of this invention to provide a concentrated composition, as described above, packaged within a stoppered, non-frangible, pressure-resistant container formed of chemically-inert material.

Furthermore, it is also a feature of this invention to provide an article of manufacture comprising in combination a plant-growth regulating composition, which contains one or more of the previously-specified phosphonic acid derivatives together with an aqueous or non-aqueous liquid medium or a pulverulent solid carrier, within a container for said composition, and instructions supplied with said container as to the manner in which the composition contained therein is to be applied to plants in order to regulate their growth.

The instructions will preferably be physi-

cally associated with the container, for instance by printing directly thereon or affixing a printed label or tag thereto. The directions will normally specify that the composition, after dilution if necessary, shall be applied broadcast to the plant-containing locus at a rate corresponding to between 0.1 and 30 pounds of the phosphonic acid derivative(s) per acre, mostly between $\frac{1}{4}$ and 16 pounds per acre, and preferably between $\frac{1}{2}$ and 4 pounds per acre. Alternatively the directions may specify application to the plant in a diluent at a concentration therein of between 1 and 48,000 parts per million, and preferably between 10 and 10,000 ppm.

In order to illustrate the biological effects of the phosphonic derivatives of this invention, there are presented below a series of Evaluations. These evaluations demonstrate the effect of the compounds of this invention in increasing yields and tillers while minimising lodging in cereals; reducing the height of annual grasses and dicotyledons; increasing yields in beans and peas; inducing flowering, particularly in pineapples; inducing fruit abscission; giving freeze resistance; and increasing the recoverable food content of plants.

EVALUATION I

This Evaluation demonstrates the use of a compound of this invention to increase crop yield. It shows that compounds of the invention can increase the fruit number and the weight of the aerial parts of *Phaseolus vulgaris* (varieties of snapbean and kidney bean) when applied in aqueous solution at the first trifoliate stage at the rate of 1.12 kg/ha.

Compound of the invention	Plant variety	Results (60 days after treatment)	
		Pods/plant	Plant Weight (grams)
pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid	Snapbean		
	Control	6	29
	treated	15	70
2-chloroethyl-phosphonic acid	Kidney bean		
	Control	20	83
	treated	25	134

In this Evaluation the treated plants were also shorter, with heavier stems, and had appreciably more lateral shoots than the controls. The effects are desirable, in that they reduce lodging and give greater crop bearing vegetation respectively.

EVALUATION II

This Evaluation demonstrates the use of a

compound of the invention to increase crop yield.

Young tomato plants (*Lycopersicon esculentum*) were sprayed at the two-leaf stage with aqueous solutions of the butyl and 2-hydroxyphenyl diester of 2-chloroethyl-phosphonic acid at a rate of 2.24 kg/ha. Inspection ten weeks later showed increased flowering as well as increased fruit yield.

Treatment	No. of Flowers and Fruit
Controls	28
Treated Plants	53

The treated plants were appreciably more branched, had many root primordia developed along the lower stem but were the same height as the controls. The increased branching indicates that the compound of this invention can indicate rooting which should result in more vigorous plants and a better up-take of water and nutrients.

compound of this invention to increase crop yield.

It shows that a representative cyclic ester of the invention, namely the pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid, can increase fruit count and weight when applied in aqueous acetone solution to *Phaseolus vulgaris* (varieties of snapbean and kidney bean) at the third trifoliate stage. It will be noted that the most effective application rate was 0.28 kg/ha.

10

EVALUATION III

This Evaluation demonstrates the use of a

Plant variety	Rate Kg/Ha.	Results 7 weeks later	
		Fruit Count	Weight (grams)
Kidney bean	Control (0)	23	100
	0.28	32	136
	0.56	27	130
Snapbean	Control (0)	42	8
	0.28	110	19
	0.56	93	11

EVALUATION IV

This Evaluation also demonstrates the use of a compound of the invention to increase potential crop yield.

Pinto bean plants (*Phaseolus vulgaris*) were

sprayed at the third trifoliate stage with aqueous alcohol solutions of the 4-chloropyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid. The results of an inspection 3 weeks later are reported below.

Treatment Rate, Kg/Ha	Leaves	Flowers
Control (0)	23	1
1.12	31	5
2.24	32	15

These results illustrate axillary stimulation, providing more potential sites for fruit.

EVALUATION V

This Evaluation also demonstrates the use of a compound of the invention to increase crop yield.

French beans, variety Dwarf bean ("The

Prince"), were treated with aqueous solutions of 2-chloroethyl-phosphonic acid at a rate of 0.5 kg/ha at the 1½—2 true-leaf stage. The crop was harvested twice and, as the following results show, an increase in yield per plant over that of the control plants was noted at the second harvest.

Treatment	Average yield per plant (gms) at 2nd harvest
Control (0)	6
2-chlorethyl-phosphonic acid	27

EVALUATION VI

This Evaluation demonstrates the use of a compound of the invention to induce flowering—that is to say, to “force” all the flower buds on the plants to bloom substantially simultaneously—in pineapples.

The following overall results were obtained when pineapple plants were inspected 62 days following spray treatment with the compounds specified below.

Compound tested and pineapple variety	Application rate lbs./acre	% flowering and induction
<u>Smooth Cayenne</u>		
Control	—	30%
2-chloroethyl-phosphonic acid	1 in 50 gallons water	100%
	2 in 50 gallons water	100%
	4 in 50 gallons water	100%
<u>Red Spanish</u>		
Control	—	25%
2-chloroethyl-phosphonic acid	2 in 200 gallons water	100%
	4 in 200 gallons water	100%
	8 in 200 gallons water	100%

Simultaneous flowering is desirable, in that it tends to results in substantially simultaneous fruiting—thus reducing the number of harvesting periods to gather the total crop.

EVALUATION VII

This Evaluation also demonstrates the use of a compound of the invention to induce flowering.

20 ml. portions of 2-chloroethyl-phosphonic acid in aqueous solution at the rates indicated below were applied to the crown of pineapple plants of the Smooth Cayenne Variety, and the following results were seen when the plants were inspected 89 days later.

Application rate (ppm)	Flower induction
Control (0)	15%
1,000	100%
10,000	100%

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EVALUATION VIII

This Evaluation demonstrates the use of other compounds of the invention to induce flowering.

5 20 ml. portions of the following phosphonic

derivatives in aqueous solution were applied at a concentration of 10,000 ppm to pineapple plants of the Red Spanish variety and the following results were obtained.

Compound	Flower induction
Bis(acid chloride) of 2-chloroethylphosphonic acid	100%
The pyrocatechol cyclic ester of 2-chloroethylphosphonic acid	100%
The mixed butyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid	100%

The use of compounds of this invention on pineapples also has other important effects. For example, it causes general growth inhibition of the plant—giving a smaller plant and allowing more plants per acre. It also inhibits the growth of the peduncle (the stem on which the fruit grows), thus helping to prevent lodging and possible fruit damage arising therefrom (sun-scorch).

20 Inspection of a pineapple plantation used as a control plot showed that only a small percentage (about 20%) of the pineapple

plants had flowered naturally in the same period.

EVALUATION IX

This evaluation demonstrates the use of the invention to increase yields and to reduce lodging.

Plots of 60 wheat plants (*Triticum aestivum*) at the four-leaf stage were treated with aqueous solutions of certain compounds of this invention, and the following results were noted when the plants were inspected four months later.

Treatment: Compound; Rate in kg/ha	Average plot wheat head weight (grams)
Control (0)	26.4
2-chloroethyl-phosphonic acid	
1.12	41.1
2.24	42.5
4.48	44.9
pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid	
1.12	38.2
2.24	40.9
4.48	42.5

The term "lodging" describes the falling over of the plant for reasons such as weak stems, heavy head, high winds and so on. It is undesirable, since it makes harvesting very difficult.

40 Moderate lodging was observed in the control wheat but none was found in the treated plants.

EVALUATION X

This Evaluation also demonstrates the use of a compound of the invention to increase yields and reduce lodging.

Winter wheat (*Triticum spp.*) plants were sprayed at early boot stage with aqueous solutions of the diphenyl ester of 2-chloroethyl-phosphonic acid; results are recorded below.

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Treatment: Rate kg/Ha	% Growth Inhibition	% Yield Increase	% Lodging
Control (0)	—	—	95.5
1.12	7.3	36.7	36.6
2.24	12.2	36.7	15.0
4.48	15.1	36.9	5.0

The % growth inhibition is a measure of reduction in stem length (plant height). It is desirable so as to prevent lodging.

- 5 The term "boot stage" describes generally that stage in a cereal crop when the ear has formed within but not separated from the stem. "Early boot stage" is the beginning of that stage, "late boot stage" the end (when the ear just protrudes from the stem).

EVALUATION XI

This Evaluation demonstrates the use of a compound of this invention to increase yields and reduce lodging.

2-chloroethyl-phosphonic acid was applied 15 to winter wheat at either the tillering stage or the early boot stage. The following was noted when the crop was harvested.

Stage of treatment	Rate Kg/Ha	Growth inhibition %	Yield, % increase	Lodging %
Tillering	Control (0)	—	—	89.1
	1	1.3	17.21	71.3
	2	2.2	38.15	58.3
	4	2.3	20.51	86.3
Early Boot	Control (0)	—	—	95.5
	1	7.3	36.76	36.6
	2	12.2	36.76	15.0
	4	15.1	36.90	5.0

- 20 The compound of this invention showed a shortening effect on the plants: the higher the rates and the later the date of application, the greater the shortening effect. Straw shortening observed after the first application was less than that obtained with the second treatment. The shortening effect after the second application became visible between the last leaf and the ear, i.e. there was hardly any space left between the last leaf and the ear. Also, all plots treated gave better yields than the untreated, this yield increase being better with the second treatment. In the early boot stage lodging was reduced considerably, i.e. the stability of wheat was increased.

- 35 Tillers are secondary stems growing from the same seed as the main stem and at the very base of that stem. The "tillering stage" is when these tillers begin to grow.

EVALUATION XII

This Evaluation demonstrates growth regulation when using a compound of this invention. It will be noticed that the time of application is not very important though early application gives greater inhibition (manifested as a reduction in internode distance and resulting in reduced lodging) than late application.

In this Evaluation, aqueous solutions of 2-chloroethyl-phosphonic acid were sprayed on winter wheat on three successive occasions operated by intervals each of the order of one month. The plots were inspected three weeks after the last application and it was noted that the overall stem lengths were shorter in the treated plants than the control. Comparison of the internodes showed that the growth inhibition effect was manifested at the

plant tip at the time of each application. Thus, the first application reduced the size of the lowest internode in the treated plants compared with the controls, the second application had the same effect on the middle internodes whereas the last application had the

same effect on the top internode. This is shown from the following data in which the distance from the lower edge of the ear to the first node is considered to be the first node distance; all measurements are in centimeters.

Treatment	Rate	First Internodal Dist.		Second Internodal Dist.		Third Internodal Dist.		Fourth Internodal
Control	—	49	11	28	10	18	5	13
2-chloroethyl-phosphonic acid	1	38	10	28	9	19	5	14
"	2	34	8	28	8	20	6	14
"	4	33	7	28	8	20	6	14

In another evaluation on winter wheat, the sensitivity of the weed *Apera spica venti* to compounds of this invention was noted.

EVALUATION XIII

This Evaluation demonstrates the use of a compound of the invention to increase crop yield.

Test plots of winter wheat (variety Genesee) were planted in September and the plots were sprayed with an aqueous solution of 2-chloroethyl-phosphonic acid in the following May when the developing grain heads were 1 mm in length. The crop was harvested in mid-July and the following results noted.

Treatment	Rate	Yield increase %
	Kg/Ha	
Control	—	—
2-chloroethyl-phosphonic acid	.28	1
	.56	17
	1.12	25
	2.24	30

EVALUATION XIV

This Evaluation demonstrates the use of a compound of the invention to increase crop yield and tillering, and to reduce lodging.

Spring wheat (variety Opal) was planted in test plots which were treated as follows. One set of test plots (I) was sprayed with an aqueous

solution of 2-chloroethyl-phosphonic acid at the pre-tillering stage and a second set (II) was treated with a similar solution at the FULLY TILLERED JOINTING stage. The plots were inspected immediately before harvesting and rated for average lodging and average number of tillers.

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The results are shown as follows:

Treatment	Plot	Dosage Kg/Ha	Yield increase %	Height Tiller Lodging %
Control	I	—	—	114 4.75 50
Compound		1.1	11	105 5.28 50
Compound		2.2	14	111 5.54 54
Control	II	—	—	106 — 47
Compound		1.1	17	99 — 36
Compound		2.2	33	89 — 12

5 When application was made at the pre-tillering stage (I) tillering was increased but where the plots were treated at the fully tillered stage (at which point the plants had produced all possible tillers) it was not, naturally, reasonable to expect an increase in tillering.

10 In other tests using 2-chloroethyl-phosphonic acid on winter wheats of different varieties (e.g. Carsten and Genessee), summer wheat, spring wheat, and some hard wheats, increase in yields were again noted, as was a beneficial

reduction effect on lodging. The same was true for other cereals particularly oats, barley, 15
rye and rice.

EVALUATION XV

This Evaluation demonstrates the use of a compound of the invention to increase crop yield and reduce plant height. 20

Cotton plants (*Gossypium hirsutum*) were sprayed when squares (the boils) were just forming, with aqueous solutions of 2 - chloroethyl-phosphonic acid. The following results were recorded ten weeks later. 25

Treatment Rate kg/Ha	Bolls/Plant	Change in plant height
Control (0)	19.1	—
1.12	29.3	+2%
2.24	24.7	-12%
4.48	26.0	-13%

30 The increased yield of cotton is apparent. The reduction in plant height is useful, being indicative of a general reduction of non-useful vegetation.

EVALUATION XVI

This Evaluation demonstrates the use of a compound of the invention to increase crop yield.

35 Barley plants (*Hordeum spp.*) were treated at the four-leaf stage with an aqueous solution of the pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid at a rate of 2.24 kg/ha. Four months later, the average weight of barley heads from 60 treated plants was 111.0 grams, whereas for the untreated plants the figure was 94 grams. This gives a yield increase of 18% 40
for the treated plants over the untreated control plants.

EVALUATION XVII

45 This Evaluation demonstrates the use of a compound of the invention to increase stem formation (tillering) and reduce overall stem height. Summer barley (variety Impala) was sprayed with aqueous solutions of 2-chloroethyl-phosphonic acid, with or without urea, at the 1½—2 leaf stage and the plants inspected some 10 weeks later. The following results were obtained, from which it will be seen that the compound of this invention — either alone or 50
with the urea — decreased the total plant height (thus decreasing any tendency toward lodging) while increasing the average number of stems per plant (thus increasing potential crop yield). 55
60

Treatment (s)		Rate Kg/Ha	Stem height (cm)	Stem average plant
Control		—	93	3.2
2-chloroethyl-phosphonic acid	—	2	87	3.4
—	urea	35	93	3.2
2-chloroethyl-phosphonic acid	urea	2+35	84	3.8
2-chloroethyl-phosphonic acid	—	4	81	4.5
2-chloroethyl-phosphonic acid	urea	4+35	79	4.3

EVALUATION XVIII

This Evaluation demonstrates the use of a compound of the invention to reduce stem height. Test plots of winter Rye were sprayed when the second node was visible with an

aqueous/acetone solution (containing a dispersing agent) of 2-chloroethyl-phosphonic acid. A month later the plots were examined and the following noted.

Treatment	Rate Kg/Ha	Stem height Cm
Control	—	110
2-chloroethyl-phosphonic acid	1	97
"	2	87
"	4	75

The reduction in stem height helps to reduce lodging tendencies.

EVALUATION XIX

This Evaluation demonstrates the use of a compound of the invention, in connection with well known herbicidally active compounds, to increase the effect of these herbicidally active compounds.

Plots of perennial grasses, mainly *Agrostis*

spp., *Agropyron repens*, *Dactylis*, *Lolium* and *Holcus mollis*, were set up and after being cut were treated with certain compounds and combinations thereof as specified below. Two months later the plots were inspected and the following results noted.

Treatment(s)		Rates, kg/ha	Score EWRC Rating System
Control		—	9
2-chloroethyl-phosphonic acid	—	4	6
—	Maleic hydrazide	4	8
2-chloroethyl-phosphonic acid	Maleic hydrazide	4+4	5
—	FENAC	2	9
2-chloroethyl-phosphonic acid	FENAC	4+2	7
2-chloroethyl-phosphonic acid	FENAC	8+2	5
—	MSMA	5	8
2-chloroethyl-phosphonic acid	MSMA	4+5	5

FENAC = 2,3,6-trichlorophenylacetic acid (as the sodium salt)

(FENAC is a Registered Trade Mark)

MSMA = monosodium acid methane arsonate.

In other treatments using mixtures of 2-chloroethyl-phosphonic acid, FENAC and MSMA (4+2+5), scores of the order of 4 were obtained. 15

The scoring method used in this table is a logarithmic score based on 9 as no effect whatsoever and 1 as complete control. This system is that adopted by the European Weed Research Council. 20

The results demonstrate that combinations of a compound of this invention and certain known herbicides act as stronger control agents than the herbicide alone. It is believed that 25

this added activity is the result of stimulation of the plant causing increased intake of the herbicide.

EVALUATION XX

This Evaluation shows the need of a compound of the invention to stimulate plant growth. 20

Mature Johnson grass (*Sorghum halepense*) was sprayed with an aqueous solution of the pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid; three weeks later, the rhizomes were dug up, weighed and dried. The results are given below. 25

Treatment: Rate, Kg/Ha	Rhizome dry weight, grams
Control (0)	1.2
1.12	4.5
2.24	4.2

The treatment also caused development of axillary buds at the crown area and along the rhizome axis. 30

EVALUATION XXI

This Evaluation shows the use of a compound of the invention to reduce stem lengths

and reduce lodging. Peas (*Pisum sativum*) were sprayed at the 9—10 trifoliate leaf stage with aqueous solutions of the 2-chloroethyl mono-ester of 2-chloroethyl-phosphonic acid. Results were recorded one month later. 35

Treatment Rate	Stem length (% decrease)	Lodging
Control (0)	—	All plants lodged.
0.45	6	Plants slightly more erect than control.
2.24	19	Most plants erect and 10 cm higher than controls
4.48	25	All plants erect and 20 cm higher than controls.

5 The results demonstrate the decrease in stem length, resulting in shorter, stronger stems and thus allowing the plants to stand erect (thus higher than the control plants).

EVALUATION XXII

10 This Evaluation demonstrates the use of a compound of the invention to increase crop yield and decrease lodging. An aqueous solution of 2-chloroethyl-phosphonic acid was sprayed on edible peas (for canning) either at the 6—9 leaflet stage, the preflowering stage or the stage at which 2 to 3 flowers had formed. Observations were made one month later and

it was found that a clear anti-lodging effect was apparent in each case. 15

The crops were later harvested and it was found that there was an overall increase in yield from the treated plants. This was more apparent at the lower rates (say 0.85 kg/ha). 20

EVALUATION XXIII

Another Evaluation performed on peas using aqueous solutions of 2-chloroethyl-phosphonic acid showed an increase in the number of pods per pea plant, the actual results being as follows. 25

Treatment	Rate kg/Ha	Average number pods/plant
Control	—	8.79
2-chloroethyl-phosphonic acid	1.12	9.95
"	2.24	8.9
"	4.48	9.41

EVALUATION XXIV

30 This Evaluation demonstrates the use of a compound of the invention to increase tillering and retard terminal growth.

35 Oat seeds (*Avena sativa*) were soaked for six hours in 50 cc of various aqueous alcohol solutions containing the pyrocatechol cyclic ester of a 2-halo-ethyl-phosphonic acid. The seeds were planted and the plants inspected seven weeks later; the results are reported

below. Economically useful biological effects—thus earlier sprouting and flowering — were observed when tubers (e.g. potato, yam and cassava) were given a soak in solutions of compounds of this invention and then planted. In the case of early potatoes especially, there seemed to be an acceleration of the plant growth which allowed the treated plants to be harvested some days earlier than the controls. 45

Oats

Treatment Rate	Observations
Control (0)	Plants Normal.
1 ppm. of phosphonic derivative	Plants 5 cm higher than controls no increase in tillering.
10 ppm.	Plants same height as controls, slight increase in number of tillers.
100 ppm.	Plants same height as controls, more tillers than at 10 ppm.
1000 ppm.	Plants slightly shorter than controls, slightly more tillers than at 100 ppm.

The results show an increase in the tiller count and hence potential yield, and show that at high concentrations there is a retardation in the terminal growth of the plant (thus reducing lodging tendencies).

compound of this invention to increase lateral branching. Rooted cuttings of privet (*Ligustrum vulgare*) were sprayed with aqueous solutions of the pyrocatechol cyclic ester of 2-chloroethyl phosphonic acid. Observations at six and sixteen weeks showed the following.

EVALUATION XXV

This Evaluation demonstrates the uses of a

Treatment	Observations	
	Six Weeks	Sixteen Weeks
Control (0)	Terminal bud growth only, no lateral bud growth.	Total Height—33 cm 9 shoots/plant
Treated with 4.48	Lateral bud growth at majority of nodes of stem; terminal growth retarded.	Total Height—45 cm 20 shoots/plant.
Treated with 8.96	Lateral bud growth observed at majority of nodes of stem in greater numbers than at 4.48 rate; terminal growth more retarded than at 4.48 rate.	Total Height—45 cm 20 shoots/plant.
Treated with 17.6	Much lateral bud growth on stem nodes; terminal growth greatly retarded.	Total Height—48 cm 22 shoots/plant.

The results seen also showed that terminal growth was retarded but not completely halted. Growth continued, in fact, later in the season for the treated plants than for the controls.

5 EVALUATION XXVI

This Evaluation shows extensive terminal growth inhibition.

- 10 Topped tobacco (*Nicotiana tabacum*) plants (plants having had the top growth removed) were treated with an aqueous solution of 2-bromoethyl-phosphonic acid at the rate of 100 mgms. per plant. Ratings made two weeks later showed no sucker growth from the buds on the top part of the treated plants, whereas the control plants (topped but not treated) had suckers developing from the top three nodes but no sucker development from basal nodes. There was some development of auxiliary buds on the basal portion of the treated plants from buds close to the soil line. This shows that the

growth inhibition effect may extend from the lead bud to lateral buds down the stem.

EVALUATION XXVII

This Evaluation demonstrates use with herbicides to control perennial grasses.

In an Evaluation using 2-chloroethyl-phosphonic acid, alone or in combination with 3-amino-1,2,4-triazole or ammonium thiocyanate, control of quackgrass (*Agropyron repens*) and bentgrass (*Agrostis tenuis*) was achieved at rates of from 2 kg/ha of 2-chloroethyl-phosphonic acid. The herbicides alone needed higher rates.

EVALUATION XXVIII

Rose (*Rosa. spp.*) varieties *Europeana (floribunda)* and *Mr. Lincoln (Hybrid-tea)* were sprayed to run-off with aqueous solutions of 2-iodoethyl-phosphonic acid prior to nursery field harvest. Observations made seven days later are as follows.

Treatment	Observations	% Defoliation
Control (0 ppm)	No abscission; foliage normal dark green.	0
500 ppm.	Initial leaves at base of plant chlorotic and abscising.	5—10
1,500 ppm.	As for 500 ppm	10—25
4,500 ppm.	All leaves abscising green.	95—100
10,000 ppm.	All leaves abscising green, some leaf desiccation.	97—100

- 45 Abscission is literally the "falling off" of the leaf, as occurs naturally in autumn. The results illustrate accelerated abscission of mature foliage, which is very useful in Nurseries, for example when the plants are stored over the winter. Leaves on the plant can rot, which is undesirable.

EVALUATION XXIX

This Evaluation shows abscission effects in apple fruit. Apple trees (*Malus domestica*: variety McIntosh) were sprayed to run-off with aqueous solutions of 2-chloroethyl-phosphonic acid just prior to normal fruit harvest. Fruit abscission noted seven and eleven days after treatment was as follows:

Treatment	% Fruit abscission		Maturity Index	
	7 days	11 days	lb/pressure	% maturity increase
Control (0 ppm.)	17	38	6.9	0
500 ppm.	66	100	4.6	34
1500 ppm.	85	100	4.5	35
4500 ppm.	89	100	4.0	42

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The results show how early abscission is induced causing the fruit to drop off the tree (50% abscission, for example, equals 50% fruit drop) and enabling harvesting of the fruit to be effected earlier.
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acceleration demonstrates the effectiveness of the phosphonic derivatives in allowing earlier harvesting.
 EVALUATION XXX
 In another apple abscission Evaluation (Malus domestica: variety Rome Beauty) were sprayed with aqueous solutions of 2-chloroethyl-phosphonic acid, and the fruit then mechanically harvested 16 days later using a tree shaker (which will remove only those fruit which are loose). The following results were noted:

Treatment	Rate (ppm)	% drop of fruit on tree before harvest	% fruit on tree removed by shaker
Control	—	2.1	81.7
2-chloroethyl-phosphonic acid	500	7.7	95.5
"	1000	22.0	98.8
"	2000	37.5	100

EVALUATION XXXI
 This Evaluation again shows the increase in rate of harvesting fruit on trees treated as opposed to trees untreated.
 30 Apple trees (variety Gravenstein) were

sprayed (when the fruit trees were beginning to mature) with aqueous solutions as specified below, and the trees and fruit were examined two weeks later. The following results were obtained:

Treatment	Rate ppm.	Fruit drop %	Fruit firmness lb/sq.in	Red colour (%)	Soluble solids (%)
Control	—	5	14.3	90.8	11.8
2-chloroethyl phosphonic acid	250	47.5	13.7	98.7	12.0
" NAA	250+10	8	12.5	97.9	11.8

NAA = naphthalene acetic acid

It will be seen that the sole use of 2-chloroethyl-phosphonic acid stimulates both loosening and maturing of the fruit. Thus the ripe fruit can be retained on the tree until needed for market.

phonic acid weer sprayed in run-off on to the secondary branches of olive trees bearing maturing fruit. At specified intervals thereafter, valuations were made to determine the force required to pluck off loosened fruit. A value comparable to 250 grams weight is considered adequate to permit the use of economical mechanical shakers without incurring undesirable tree damage.

EVALUATION XXXII
 This Evaluation demonstrates the increase in pickability of fruit on trees treated with a compound of this invention.
 Aqueous solutions of 2-chloroethyl-phos-

Inspection interval after spray	Control Rate			
	0 ppm	1000 ppm	2000 ppm	4000 ppm
3 days	521	406	505	427
9 days	467	451	332	162
14 days	403	111	192	92
17 days	378	105	74	43

It will be seen from these results that loosening of fruit was best achieved after a week or so of treatment. At 4000 ppm., for example, mechanical harvesting was useful after 9 days. In each case, however, the treated plants required less force than the controls to pluck off the fruit. The use of compounds of this invention at rates lower than 1000 ppm and in combination with senescence retardants are also possibilities and may be useful to remove fruit without causing leaf removal.

EVALUATION XXXIII

This Evaluation demonstrates the use of a compound of the invention in the "ripening" of citrus fruits.

Orange trees (*Citrus sinensis*): variety Valencia, and tangerine trees (*Citrus reticulata*), variety Robinson, were sprayed with aqueous solutions of the butyl and 2-hydroxyphenyl diester of 2-chloroethyl-phosphonic acid. Observations are recorded below:

Treatment	% Green	Colour promotion % Degreened.
0 (Control)	100	0
100 ppm	0	100
500 ppm	0	100
5000 ppm	0	100

Oranges for example are usually "stored" on the tree, but they can turn green even though already ripe and orange. In order to make them acceptable to the public, therefore, it is necessary to de-green them. These results demonstrate this de-greening.

This effect is of economic importance as unripe fruit are imported into European and Scandinavian countries and then artificially ripened before distribution.

EVALUATION XXXV

This Evaluation demonstrates use of a compound of the invention to increase sugar beet crop yield.

2-chloroethyl-phosphonic acid was sprayed in aqueous solution to sugar beet twice, at an interval of three weeks. The beets were inspected six weeks after the second treatment and the results are shown below:

Treatment	Increase in yield	Increase in recoverable sugar per acre
Control	—	—
0.9 kg/ha (0.75 lb/acre)	+20%	+5%

25

The valuable increases in yield and in recoverable sugar are apparent.

Johnsongrass (*Sorghum halepense*) plants were sprayed with aqueous solutions of 2-chloroethyl-phosphonic acid just before the kore head emerged from the sheath. Observations 12 days later are recorded below:

EVALUATION XXXVI

This Evaluation again shows the use of a compound of this invention in combination with a known herbicide.

Treatment	Observations
Control (no treatment)	Flowering 100% ,seed heads 100% developed. Plant foliage dark green, terminal shoots vigorous. Little subsurface lateral bud development. Terminals of rhizomes active near soil surface.
Treated with 2.24 kg/ha of phosphonic derivative	Flowering inhibited 35%; seed heads malformed, abortion 50%; panicles failed to emerge. Terminal shoots active but leaf tips exhibiting die-back. Subsoil, numerous lateral shoots at the nodes varying in size from 0.5 to 4 cm. Unsprouted rhizome buds were normal.
Treated with 4.48 kg/ha of phosphonic derivative	Flowering inhibited 95%, emerged seed heads aborted and malformed; shoot tips exhibited die-back and terminal shoots dormant; numerous subsoil lateral shoots at the nodes, shoots were active and some had grown 5 to 8 cm; growth stopped when terminal bud formed.
Treated with 4.48 kg/ha of aminotriazole alone	Flowering inhibited 65%; seed heads developed normally; plants shorter and foliage and stems green. Numerous basal shoots; some subsoil lateral bud development. Rhizome condition was vigorous.
Treated with 2.24 kg/ha of phosphonic derivative +4.48 amino-triazole	Flowering inhibited 100%; no seed head development; plants shorter, foliage brown, bud stems green. Some basal shoots had a little green foliage. The ground rhizomes were small in diameter and subsoil the base showed little or no rhizome development. Some of the terminals near the surface that had developed as laterals were dead. Although other terminal rhizome buds alive, they were of low vigor.

There was a decrease in flower and seed head development when the phosphonic derivative was applied alone. When the phosphonic derivative was applied with aminotriazole, flowering and seed head development were 100% inhibited, and the results demonstrate an interaction between the phosphonic derivative and aminotriazole resulting in improved

kill of lateral buds and reduction of rhizome vigor.

EVALUATION XXXVII

This Evaluation demonstrates use to give increased branching.

Ornamental shrubs were sprayed to run-off with aqueous solutions of 2-chloroethyl-phosphonic acid and the plants were inspected 3 months later and the following noted:

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Shrub	Treatment	Branch (no.)	Height (cm)
Chrysanthemum (variety Gipsy)	Control (0)	—	100
	100 ppm	2	97
	500 ppm	3	87
	1000 ppm	20	38
Carnation (pink)	Control (0)	4	20
	100 ppm	5	25
	1000 ppm	7	38
Fuchsia	Control (0)	21	21
	100 ppm	33	23
	1000 ppm	31	26

5 It will be seen that in general the treated plants were more highly branched than the control plants, thus giving more potential flower sites. It will also be seen that the chrysanthemum plants' heights were reduced.

EVALUATION XXXVIII
In another "branching" Evaluation an aqueous solution of a compound of this invention were sprayed to run-off on azalea plants. 10
Two months later the plants were inspected and the following noted.

Treatment Rate	Observation
1 kg/ha	Bud formation was stimulated and there were many lateral shoots
2 kg/ha	Very many lateral shoots close to plant top

Evaluations performed using lower rates gave good flower induction.

15 EVALUATION XXXIX
This Evaluation shows the use of a compound of the invention to increase germination rates.

Lettuce (*Lactuca sativa*) seeds were placed

in petri dishes on filter paper saturated with aqueous solutions of the pyrocatechol cyclic ester of 2-chloroethyl-phosphonic acid. Seeds were allowed to germinate in the dark at 25°C for 24 hours. Observations are recorded below: 20

Treatment	% Germination
Control (0)	13.1
10 ppm	12.3
100 ppm	13.3
1000 ppm	31.3

EVALUATION XL

This Evaluation demonstrates the use of a compound of the invention to impart freeze damage resistance.

- 5 Seedling beans (*Phaseolus vulgaris*); variety Blue Lake, 2½ weeks old, were sprayed with aqueous solutions of 2 - chloroethyl - phosphonic acid.

Eleven days later the plants were pre-cooled at +2° C for one hour and then kept at -5½° C for 2 hours and twenty minutes. The frozen plants were then cultured in a greenhouse and the following data was recorded.

10

Treatment	% Plants surviving freeze
Control (0)	0
200 ppm	100 — no damage
2000 ppm	100 — no damage

15

EVALUATION XLI

This Evaluation also shows freeze damage resistance.

- 20 Apple codlings (*Malus domestica*) variety Red Delicious, two weeks old were sprayed with an aqueous solution of 2 - chloroethyl - phosphonic acid.

Eighteen days later the plants were pre-cooled at +2° C for one hour and then kept at -6° C for 2 hours and thirty minutes. The frozen plants were then cultured and the following data recorded.

25

Treatment	% Plants surviving freeze
Control	0
200 ppm	100

It is apparent from the results of the foregoing evaluations that the phosphonic derivatives of this invention are capable of imparting a wide variety of plant growth regulating responses.

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EVALUATION XLII

- 35 An aqueous solution of 2 - chloroethyl-phosphonic acid was sprayed on to growing rice (*Oryza sativa*) and the plots were later inspected for tillers. The following results were obtained.

Rate (ppm)	Effective tillers
0	100
62	113
125	118

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The increase in tillers at the very low rates of treatment is to be noted.

EVALUATION XLIII

- 45 Cucumber plants were sprayed with an aqueous solution of 2 - chloroethyl - phosphonic acid at the 1 - true leaf stage. They were then inspected at the 13 - true leaf stage, and the following noted.

Rate (ppm)	No. female flowers
0	2—3
62	13
250	One every node.

50

The increase in flowers is to be noted at the low rates of treatment. Little or no growth retardation was observed at these rates.

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EVALUATION XLIV

French beans variety Dwarf bean "the Prince" were treated with aqueous solutions of 2 - chloroethyl - phosphonic acid at the rates indicated at the 1½—2 true leaf-flower bud stage. The following increases in total yield were noted.

60

Treatment	Total yield per plant (gms)
Control	41
0.25	46
0.50	48

65

EVALUATION XLV

20 ml portions of 2 - chloroethyl phosphonic acid in aqueous solution were applied at rates of up to 10,000 ppm to ornamental plants of the Bromeliadaceae family, and increases in flower induction were observed.

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EVALUATION XLVI

2 - chloroethyl - phosphonic acid was sprayed as an aqueous solution on to winter wheat infested with *Apera spica venti*. Inspection of the plots later showed suppression of the seed head formation of the *Apera*, in addition to the beneficial effects on the winter wheat.

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Height (cm)

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The biological evaluations given above have been chosen from the extensive data available more to illustrate the range of plant responses attainable in a wide variety of plants in accordance with this invention than to illustrate the plant growth regulating activities of a broad range of the phosphonic acid derivatives. However, it should be noted that essentially similar effects can be secured with other phosphonic acid derivatives herein disclosed, notably those specifically named, though naturally the rate of application may need appropriate adjustment.

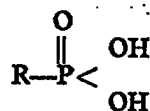
In order to illustrate the compositions of this invention reference is first made to the biological evaluations set forth above. It will be noted that aqueous solutions of 2 - chloroethyl phosphonic acid, its pyrocatechol cyclic ester, its mixed butyl and 2 - hydroxy - phenyl cyclic ester, its 4 - chloro - pyrocatechol cyclic ester, its 2 - chloroethyl monoester, its bis-(phenyl) diester, as well as 2 - bromoethyl phosphonic acid and 2 - iodoethyl phosphonic acid are used. As also indicated above, the phosphonic acid derivatives specified in the biological evaluations may be replaced by other previously-named phosphonic acid derivatives. The aqueous solutions may as also indicated above contain organic co-solvents such as alcohol and/or acetone and/or methyl - ethyl-ketone. Although not indicated in the biological evaluations, the aqueous solutions employed usually contained minor quantities of acetic acid to adjust their pH value to less than 5, and in at some cases a buffering agent was also present. The aqueous solutions as applied to the plants were prepared by diluting concentrates with water. The concentrates contained approximately 10—15% by weight of the phosphonic acid derivative(s), and were stored in stoppered polyethylene or polypropylene containers, marked with instructions to dilute the contents with water to yield the desired concentrations in the solutions for application to the plants and/or soil.

The phosphonic acid derivatives used in the processes and compositions of this invention are in some cases new compounds, but we make no claim herein to them as such. Equally, we make no claim herein to any processes for the preparation of these compounds, whether previously known or unknown, as it is believed that the preparation of such phosphonic acid derivatives is in general within the competence of any skilled chemist. Certain advantageous processes for the preparation of the mixed diesters have been described in British Patent Application Nos. 8757/68 and 8758/68. The processes there described may be briefly summarized as the transesterification of a substituted or unsubstituted catechol cyclic ester of a 2 - haloalkyl phosphonic acid (obtained as described by Kabachnik *et al.*, *Izvest. Akad. Nauk. SSSR*, o.k.h.n., (1947),

page 97 — *Chem. Abstracts*, 42, 4132e) at room or slightly elevated temperatures not exceeding 60° C.

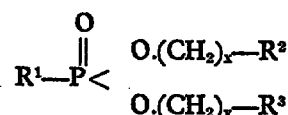
WHAT WE CLAIM IS:—

1. A process for regulating plant growth, in which there is applied to the plant an effective amount of a plant growth regulator comprising one or more phosphonic acid derivatives conforming to the general formula



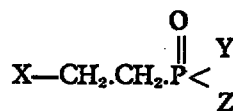
where R is a vinyl, allyl, haloethyl, halopropyl, methoxy - ethyl, carboxymethyl or phosphono-ethyl group, and/or the corresponding acid chlorides and/or anhydrides and/or amides and/or hydrolyzable mono- and di - esters and/or salts thereof.

2. A process for regulating plant growth in which there is applied to the plant an effective amount of a plant growth regulator comprising one or more phosphonic acid derivatives conforming to the general formula



in which one of x and y is 0 and the other is 0 or 1; R^1 is a vinyl, allyl, haloethyl, halopropyl, methoxyethyl, carboxymethyl or phosphono - ethyl group; R^2 is a hydrogen atom or a substituted or unsubstituted phenyl group; and R^3 is a hydrogen atom or a substituted or unsubstituted phenyl group or a halogen-substituted or unsubstituted, saturated or unsaturated hydrocarbon chain containing from 2 to 12 carbon atoms.

3. A process for regulating plant growth comprising applying to the locus to be treated an effective amount of a plant growth regulator comprising one or more (halo/phosphono) - ethyl phosphonic acid derivatives conforming to the general formula



where X is a halogen atom or a phosphono —PO(Y) Z group; Y is a chlorine atom or an —OR⁴ group; R^4 is a hydrogen atom, a salt-forming cation, a substituted or unsubstituted aryl-, arylmethylene-, heterocyclyl- or heterocyclylmethylene group, or the X·CH₂·CH₂·PO(Z)-group; and Z is defined as (but not necessarily identical to) Y or is an oxyhydrocarbon group wherein the hydrocarbon chain may be substituted or un-

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The biological evaluations given above have been chosen from the extensive data available more to illustrate the range of plant responses attainable in a wide variety of plants in accordance with this invention than to illustrate the plant growth regulating activities of a broad range of the phosphonic acid derivatives. However, it should be noted that essentially similar effects can be secured with other phosphonic acid derivatives herein disclosed, notably those specifically named, though naturally the rate of application may need appropriate adjustment.

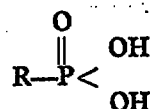
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The phosphonic acid derivatives used in the processes and compositions of this invention are in some cases new compounds, but we make no claim herein to them as such. Equally, we make no claim herein to any processes for the preparation of these compounds, whether previously known or unknown, as it is believed that the preparation of such phosphonic acid derivatives is in general within the competence of any skilled chemist. Certain advantageous processes for the preparation of the mixed diesters have been described in British Patent Application Nos. 8757/68 and 8758/68. The processes there described may be briefly summarized as the transesterification of a substituted or unsubstituted catechol cyclic ester of a 2 - haloalkyl phosphonic acid (obtained as described by Kabachnik *et al.*, *Izvest. Akad. Nauk. SSSR*, o.k.h.n., (1947),

page 97 — *Chem. Abstracts*, 42, 4132e) at room or slightly elevated temperatures not exceeding 60° C.

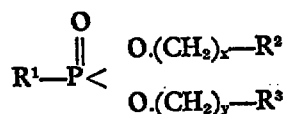
WHAT WE CLAIM IS:—

1. A process for regulating plant growth, in which there is applied to the plant an effective amount of a plant growth regulator comprising one or more phosphonic acid derivatives conforming to the general formula



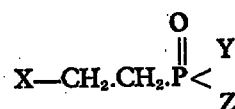
where R is a vinyl, allyl, haloethyl, halopropyl, methoxy - ethyl, carboxymethyl or phosphonoethyl group, and/or the corresponding acid chlorides and/or anhydrides and/or amides and/or hydrolyzable mono- and di - esters and/or salts thereof.

2. A process for regulating plant growth in which there is applied to the plant an effective amount of a plant growth regulator comprising one or more phosphonic acid derivatives conforming to the general formula



in which one of x and y is 0 and the other is 0 or 1; R¹ is a vinyl, allyl, haloethyl, halopropyl, methoxyethyl, carboxymethyl or phosphono - ethyl group; R² is a hydrogen atom or a substituted or unsubstituted phenyl group; and R³ is a hydrogen atom or a substituted or unsubstituted phenyl group or a halogen-substituted or unsubstituted, saturated or unsaturated hydrocarbon chain containing from 2 to 12 carbon atoms.

3. A process for regulating plant growth comprising applying to the locus to be treated an effective amount of a plant growth regulator comprising one or more (halo/phosphono) - ethyl phosphonic acid derivatives conforming to the general formula



where X is a halogen atom or a phosphono —PO(Y) Z group; Y is a chlorine atom or an —OR⁴ group; R⁴ is a hydrogen atom, a salt-forming cation, a substituted or unsubstituted aryl-, arylmethylene-, heterocycyl- or heterocycylmethylene group, or the X.CH₂.CH₂.PO(Z)-group; and Z is defined as (but not necessarily identical to) Y or is an oxyhydrocarbon group wherein the hydrocarbon chain may be substituted or un-





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- substituted, saturated or unsaturated; or Z and R⁴ together form an —O—O— , $\text{—O—CH}_2\text{—O—}$, —CO—O—O— or —CO—NH—O— linkage, where O represents a divalent, substituted or unsubstituted benzene or heterocyclic ring.
- 5 4. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes 2 - chloroethyl phosphonic acid.
- 10 5. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the anhydride of 2 - chloroethyl phosphonic acid.
- 15 6. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the bis-(acid chloride) of 2 - chloroethyl - phosphonic acid.
- 20 7. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the pyrocatechol cyclic ester of 2 - chloroethyl phosphonic acid.
- 25 8. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the 4 - chloro-pyrocatechal cyclic ester of 2 - chloro - ethyl phosphonic acid.
- 30 9. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed ethyl and 2 - hydroxy - phenyl diester of 2 - chloroethyl phosphonic acid.
- 35 10. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed butyl and 2 - hydroxy - phenyl diester of 2 - chloroethyl phosphonic acid.
- 40 11. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed propynyl and 2 - hydroxy - phenyl diester of 2-chloroethyl phosphonic acid.
- 45 12. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the bis - (penta-chloro - phenyl) diester of 2 - chloroethyl phosphonic acid.
- 50 13. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the 2 - chloroethyl monoester of 2 - chloroethyl phosphonic acid.
- 55 14. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the bis - (phenyl) diester of 2 - chloroethyl phosphonic acid.
- 60 15. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the tetrachloro-pyrocatechol cyclic ester of 2 - chloroethyl phosphonic acid.
- 65 16. A process as claimed in any of the preceding claims in which the plant growth regulator is or includes the saligen cyclic ester

of 2 - chloroethyl phosphonic acid.

17. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the salicylic acid cyclic ester of 2 - chloroethyl phosphonic acid.

18. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the 3 - hydroxy-phenyl monoester of 2 - chloroethyl phosphonic acid.

19. A process as claimed in any of the preceding claims in which the plant growth regulator is or includes the bis - (2 - oxo - pyrrolidinyl - methyl) diester of 2 - chloroethyl phosphonic acid.

20. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed phenyl and o - hydroxy - phenyl diester of 2 - chloroethyl phosphonic acid.

21. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the o - hydroxy-phenyl monoester of 2 - chloroethyl phosphonic acid.

22. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed isopropyl and 2 - hydroxy - phenyl diester of 2-chloroethyl phosphonic acid.

23. A process as claimed in any of the preceding claims in which the plant growth regulator is or includes the mixed octyl and 2-hydroxy - phenyl diester of 2 - chloroethyl phosphonic acid.

24. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the salicylic acid cyclic ester of 2 - chloroethyl phosphonamidic acid.

25. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed hexadecyl and 2 - hydroxy - phenyl diester of 2-chloroethyl phosphonic acid.

26. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the mixed tri-decyl and 2 - hydroxy - phenyl diester of 2-chloroethyl phosphonic acid.

27. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes the 2,3 - pyridine - diol cyclic ester of 2 - chloroethyl phosphonic acid.

28. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes 2 - bromoethyl phosphonic acid or one of its derivatives.

29. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes 2 - iodoethyl phosphonic acid or one of its derivatives.

30. A process as claimed in any of the preceding claims in which the plant growth regu-

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lator employed is or includes 2 - fluoroethyl phosphonic acid or one of its derivatives.

31. A process as claimed in any of the preceding claims in which the plant growth regulator employed is or includes 2 - phosphonoethyl phosphonic acid or one of its derivatives.

32. A process as claimed in any of the preceding claims in which the plant growth regulator is applied to the plant-containing locus at a rate from 0.1 lbs./acre to 30 lbs./acre.

33. A process as claimed in claim 32, in which the application rate is from $\frac{1}{4}$ lb./acre to 16 lbs./acre.

34. A process as claimed in claim 32 or 33, in which the application rate is from $\frac{1}{4}$ lb./acre to 4 lbs./acre in aqueous solution.

35. A process for the regulation of plant growth as claimed in any of the preceding claims in which the plant growth regulator is applied to the plant in aqueous solution containing a concentration of the phosphonic acid derivative(s) of from 1 to 48,000 parts per million.

36. A process for the regulation of plant growth as claimed in claim 35, in which the concentration is from 10 to 10,000 parts per million.

37. A process for the regulation of plant growth as claimed in any of the preceding claims and substantially as herein described.

38. A process for the regulation of plant growth as claimed in claim 1 and substantially as herein described with reference to the foregoing Biological Evaluations.

39. A process for the regulation of plant growth as claimed in claim 2 and substantially as herein described with reference to the foregoing Biological Evaluations.

40. A process for the regulation of plant growth as claimed in claim 3 and substantially as herein described with reference to the foregoing Biological Evaluations.

41. A plant growth regulating composition for use in the process claimed in any of claims 1 to 40, which comprises one or more of the plant growth regulators as defined in any of claims 1 to 31 in a concentration of from 1 to 48,000 parts per million in a liquid solvent or dispersion medium or in a pulverulent and/or granular solid carrier.

42. A plant growth regulating composition for use in the process claimed in any of claims 1 to 40, which comprises one or more of the plant growth regulators as defined in any of claims 1 to 31 in a concentration of from 10 to 10,000 parts per million in a liquid solvent or dispersion medium or a pulverulent and/or granular solid carrier.

43. A plant growth regulating composition in concentrate form, intended for dilution before application to the plants in accordance with the process of any of claims 1 to 40, which comprises one or more of the plant growth regulators as defined in any of claims

1 to 31 in a concentration of from 10% to 30% by weight.

44. A plant growth regulating composition as claimed in any of claims 41 to 43, which also contains one or more surfactants and/or dispersing agents and/or emulsifiers and/or penetrants and/or sequestrants and/or stabilizers.

45. A plant growth regulating composition as claimed in any of claims 41 to 44, which also contains one or more other plant growth regulators.

46. A plant growth regulating composition as claimed in any of claims 41 to 45 which also contains one or more herbicides.

47. A plant growth regulating composition as claimed in any of claims 41 to 46, in which the liquid solvent medium is water containing organic co-solvent(s).

48. A plant growth regulating composition as claimed in claim 47, in which the co-solvent is or includes ethyl alcohol, acetone or methyl - ethyl - ketone.

49. A plant growth regulating composition as claimed in any of claims 41 to 48, which contains an acid in an amount sufficient to impart thereto a pH value in the presence of water of 5 or less.

50. A plant growth regulating composition as claimed in any of claims 41 to 48, which contains a buffering agent to maintain the pH value of the composition in the presence of water at 5 or less.

51. A concentrated plant growth regulating composition as claimed in any of claims 41 to 50 and intended for dilution to operative concentration before application to plants, which comprises from 10% to 30% by weight of one or more of the plant growth regulators as defined in any of claims 1 to 31 packaged within a stoppered, non-frangible, pressure-resistant container formed of chemically-inert material.

52. An article of manufacture comprising in combination a plant growth regulating composition as claimed in any of claims 41 to 51, a container for said composition, and instructions physically associated with said container as to the manner in which the composition contained therein is to be applied to plants in order to regulate their growth.

53. An article of manufacture as claimed in claim 52, in which said instructions specify that the composition, optionally after dilution, shall be applied to the plant-containing locus at a rate corresponding to between 0.1 and 30 lbs. of the plant growth regulators as defined in any of claims 1 to 31 per acre.

54. An article of manufacture as claimed in claim 53, in which the specified application rate is between $\frac{1}{4}$ and 16 lbs. per acre.

55. An article of manufacture as claimed in claim 53 or 54, in which the specified application rate is between $\frac{1}{4}$ and 4 lbs. per acre.



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56. An article of manufacture as claimed in claim 52, in which said instructions specify that the composition, after dilution if necessary, shall be applied to the plant in a diluent at a concentration therein of between 1 and 48,000 parts per million.
57. An article of manufacture as claimed in claim 56, in which the specified concentration is between 10 and 10,000 parts per million.

58. An article of manufacture as claimed in any of claims 52 to 57, wherein said instructions are substantially in accordance with the directions hereinbefore set forth.

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