

PATENT SPECIFICATION

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(54) LATEX STIMULATION

(71) We, AMCHEM PRODUCTS, INC., a Corporation organised and existing under the Laws of the Commonwealth of Pennsylvania, 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 relates to latex stimulation, and concerns in particular a novel method of stimulating the flow of latex from rubber trees.

It is well known to extract latex from growing rubber plants by selectively removing bark from the plant and allowing the latex (sap) to drain into a strategically placed vessel. Heretofore, certain agents have been employed to stimulate or increase the flow of latex, the most widely used of which is 2,4,5-trichlorophenoxyacetic acid in small amounts.

The general practice of tapping a rubber tree (*Hevea brasiliensis* in particular) involves the making of special cuts directly through the bark for a portion of the circumference of the tree. Usually, a spiral cut is formed in about one-third to one-half of the tree circumference, and such a cut is identified for convenience as an "S/3" or "S/2" cut, as appropriate. A tree cut in this way may be tapped every second or third day, and this tapping frequency is identified for convenience as a "d/2" or "d/3" tapping, as appropriate. Thus, a tree with a spiral cut extending for 120° [one-third of the way round the tree (S/3)] that is tapped every second day (d/2) would be designated "S/3.d/2".

From time to time new spiral cuts are made in the tree, and the old cuts are allowed to rest (so that eventually there is a regrowth of bark over the old cuts). At a later time, new cuts of bark will be made in the vicinity of the old cuts, depending upon whether the old

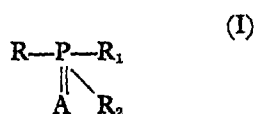
cut covered one-third, one-half or more of the tree diameter. With increasing tree age, the latex yield drops, and ultimately the tree becomes dry or gives such a low yield that it is no longer economical to work.

All trees have an optimum period in their life — a period when their latex yield is consistently high — but even in this optimum period it is found that latex flow from a particular cut will sooner or later stop. It is believed that this stoppage is largely dependent upon the tendency of latex vessels within the tree to plug (or get blocked up). For many years, however, it has been recognised that treating the tree with ethylene can restore latex flow — probably by dissolving, retarding or delaying the formation of a plug or a plugging tendency.

The desirability of an ethylene response or an ethylene-type response in many plants has been appreciated for many years (see for example, "Plant Biochemistry" by James Bonner and J. E. Varner (1965), pages 641 to 664). Indeed, ethylene has been used in gaseous form for the ripening of bananas, and to stimulate flower initiation in pineapples (see "Hormonal Control of Plant Growth" by N. S. Parihar (1964), pages 69 to 79).

The mechanism by which ethylene (and other, similar gases) affect the growth cycle of plants is far from fully understood, but it is clear that they do play a role. The method of latex stimulation of the invention involves the use of particular compounds which can break down to give ethylene, and — though there is no intention to limit the present invention to this or any other theory — it is believed that these compounds are effective for that reason.

In one aspect, therefore, this invention provides a method for the stimulation of latex flow in rubber trees, in which there is applied to the tree a phosphonic acid derivative of the general formula:



wherein:

R represents either a halo-ethyl or a phosphono-ethyl group;

5 A represents an oxygen or sulphur atom; and

1) R₁ and R₂, which are the same or different, each represent a chlorine atom, a hydroxy group or a mercapto group; or

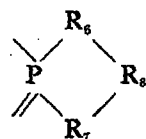
10 2) R₁ and R₂, which are same or different, are each an —AR₃ group or an —A—CH₂R₃ group (wherein A is as defined heretofore, and each R₃, which are the same, represents a substituted or unsubstituted aryl group or a heterocyclic group); or

15 3) R₁ and R₂, which may be the same or different, are each an —AR₄ group or an —A—CH₂R₄ group (wherein A is as defined hereinbefore, and the two R₄ groups are different, and each represents a hydrogen atom,

20 a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a heterocyclic group, an alkene group or an alkyne group, provided that at least one R₄ group represents a hydrogen atom, a substituted or unsubstituted aryl group, or a heterocyclic group); or

25 4) one of R₁ and R₂ is an —AR₅ group and the other is an —A.P(=A)(AR₅).R group (wherein A and R are as defined hereinbefore, and each R₅ group, which may be the same or different, represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a heterocyclic group, and wherein R is as defined hereinbefore); or

35 5) R₁ and R₂, together with the phosphorus atom, represent the cyclic group



40 (wherein one of R₆ and R₇ is —A— and the other is —A—, —CA—A— or —CANH—, A is as defined hereinbefore, and R₆ represents a divalent phenylene or substituted or unsubstituted heterocyclic ring), or a salt, amide or anhydride of any appropriate such phosphonic acid derivative.

45 General formula I includes within its scope the compound 2-chloroethyl-phosphonic acid. No claim is made herein to the use of this particular compound (because the use thereof, or the arc of any compound capable of releasing ethylene into the tree's tissues, in a low intensity tapping system, has already been described and claimed in the Specification of our Letters Patent No. 1,293,934).

The term "halo" used herein means the familiar halogens, i.e., fluorine, chlorine, bromine and iodine.

Preferred groups for the substituent R are the haloethyl groups, especially the 2-bromoethyl and 2-iodoethyl groups. 60

Preferred half-esters of the phosphonic acid moiety are the 2-chloroethyl mono-ester and the *o*-hydroxyphenyl mono-ester. Preferred diesters include the diphenyl and the *bis*-(2-oxo-1-pyrrolidinylmethyl) esters, and preferred mixed esters are the 2-hydroxyphenyl ester with an alkyl, alkenyl or aryl radical (for example, ethyl, *isopropyl*, propynyl, butyl, octyl, hexadecyl or phenyl). 65 70

The preferred aryl groups are monocyclic, though bi- or polycyclic aryl groups may be used.

The term "alkyl" as used herein means straight, branched and cyclic alkyl groups—thus, for example, methyl and ethyl, *iso*-propyl and *t*-butyl and *cyclopentyl* and *cyclohexyl*. Preferred alkyl groups are those having not more than 18 carbon atoms (above this range, the derivatives are less soluble). 75 80

Preferred cyclic esters are those formed with pyrocatechol or mono- or polyhalopyrocatechol derivatives (for example, 4-chloropyrocatechol or tetrachloropyrocatechol), those formed with salicylic acid, those formed with saligenin, and those formed with 2,3-pyridinediol. 85

The acid chlorides are also preferred derivatives.

In the cases set forth hereinabove, the substituents A are oxygen atoms. However, each substituent A may also be a sulphur atom, so that the compounds are derivatives of phosphonothionic acid or (when both R₁ and R₂ is a mercapto group) phosphonotrithioic acid. When R₁ and R₂ are each mercapto groups and A is an oxygen atom, the compounds are derivatives of phosphonodithiodic acid. The present invention further contemplates the use of the functional derivatives of the foregoing sulphur acids including acid chlorides, amides and half, full and cyclic esters. Nevertheless, the compounds wherein A is an oxygen atom are in general preferred. 90 95 100

In addition to the foregoing, certain amides of 2-chloroethylphosphonic acid are preferred in the methods of the present invention, these being 2-chloroethylphosphonic acid diamide and the N-alkyl amides (for example, N,N'-dimethyl 2-chloroethylphosphonic acid diamide and N,N,N',N'-tetramethyl 2-chloroethylphosphonic acid diamide). 105 110

Specific preferred phosphonic acid derivatives usable in the method of the present invention are: 115

- the *bis*(acid chloride) of 2-chloroethylphosphonic acid;
- the pyrocatechol cyclic ester of 2-chloroethylphosphonic acid;
- the 4-chloropyrocatechol cyclic ester of 2- 120

chloroethylphosphonic acid;
 the mixed ethyl and 2-hydroxyphenyl diester
 of 2-chloroethylphosphonic acid;
 the mixed butyl and 2-hydroxyphenyl diester
 of 2-chloroethylphosphonic acid;
 the mixed propynyl and 2-hydroxyphenyl di-
 ester of 2-chloroethylphosphonic acid;
 the 2-chloroethyl monoester of 2-chloro-
 ethyl phosphonic acid;
 2-bromoethylphosphonic acid;
 the *bis*(phenyl)-ester of 2-chloroethyl-
 phosphonic acid;
 the tetrachloropyrocatechol cyclic ester of
 2-chloroethylphosphonic acid;
 2-iodoethylphosphonic acid;
 the saligenin cyclic ester of 2-chloroethyl-
 phosphonic acid;
 the salicylic acid cyclic ester of 2-chloro-
 ethylphosphonic acid;
 phosphonoethyl-phosphonic acid;
 phosphonoethylthioethylphosphonic acid;
 the 3-hydroxyphenylmonoester of 2-chloro-
 ethylphosphonic acid which exists in poly-
 meric form);
 the *bis*(2-oxo-pyrrolidinylmethyl) ester of 2-
 chloroethylphosphonic acid;
 the *o*-hydroxyphenyl monoester of 2-chloro-
 ethylphosphonic acid;
 the mixed *isopropyl* and 2-hydroxyphenyl
 diester of 2-chloroethylphosphonic acid;
 2-fluoroethylphosphonic acid;
 the mixed octyl and 2-hydroxyphenyl diester
 of 2-chloroethylphosphonic acid;
 the mixed hexadecyl and 2-hydroxyphenyl
 diester of 2-chloroethylphosphonic acid;
 the mixed tridecyl and 2-hydroxyphenyl di-
 ester of 2-chloroethylphosphonic acid;
 2-chloroethylphosphonic anhydride;
 2-chloroethylbutylester, 2-hydroxyphenyl-
 ester of phosphonic acid;
 2-chloroethyl-2-chloroethyl ester of phos-
 phonic acid and 2-chloroethyl-phosphono-
 thionic acid, -phosphonotrithioic acid and
 -phosphonodithioic acid.
 Other useful phosphonic acid derivatives
 are:
 the salicylic acid cyclic ester of 2-chloro-
 ethyl-phosphonoamidic acid;
 the mixed phenyl and 2-hydroxyphenyl di-
 ester of 2-chloroethylphosphonic acid;
 2-chloroethyl-dichloro-phosphine;
 the *bis* (pentachlorophenyl) ester of 2-
 chloroethyl-phosphonic acid;
 the 2,3-pyridinediol cyclic ester of 2-
 chloroethylphosphonic acid;
 2-chloroethyl-thiophosphonic acid (and its
 2-bromo-, 2-fluoro- and 2-iodo analogues);
 and the
 2 - chloroethyl - 2,3 dibromo - 4 -
 hydroxy 2 butenyl phosphonic acid ester
 polymer.
 Salts of the phosphonic acid derivatives
 may be used. Examples of such salts include
 the sodium, aluminium, zinc, potassium and
 lithium salts.

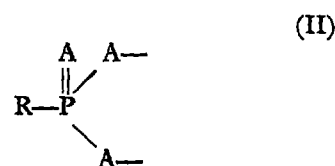
It is known that certain of the hereinabove
 mentioned phosphonic acid compounds will
 polymerize; such compounds are in general
 usable whether in monomeric or polymeric
 form.

The phosphonic acid derivatives used in the
 method of the present invention are soluble, in
 varying degrees, in water; thus they can be
 applied to the trees as aqueous solutions. Co-
 solvents may be employed where necessary,
 and in some cases—for instance, when using
 the *bis* (acid-chloride) of 2-chloroethyl-
 phosphonic acid—an organic solvent may be
 used.

Acetone and methyl ethyl ketone may be
 employed as organic solvents or co-solvents.
 In general any liquid medium may be used
 provided that it is not toxic to the plant. Other
 media, including solids (like talc), may also be
 employed.

Application rates suitable for use in the
 method of this invention should preferably be
 at least 0.15 gms (free acid equivalent) per
 tree, and advantageously at least 0.30 gms
 (free acid equivalent) per tree.

It is believed that the latex stimulating
 activity of the phosphonic acid derivatives
 resides in the



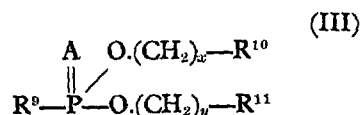
anion, and that any derivative capable of
 releasing this anion in, on or around the tree
 under treatment will display the desired latex-
 stimulating activity.

The phosphonic acid derivatives used in the
 practice of the present invention will include
 both compounds which hydrolyze very readily
 as well as compounds which hydrolyze only
 with difficulty (perhaps owing to steric hin-
 drance). Moreover, there are derivatives which
 in the laboratory can be hydrolyzed only with
 difficulty, yet which apparently can be meta-
 bolized by the plant and hydrolyzed by its
 enzymatic systems quite readily.

The phosphonic acid derivatives employed
 in the practice of the present invention should
 preferably be compounds known to be readily
 hydrolyzable, either in the laboratory or in
 the plant under treatment. The ability of any
 phosphonic acid derivative to be used for
 preference in the practice of the present inven-
 tion may initially be determined in the green-
 house by testing the derivative to determine
 its power to produce epinasty in tomato plants,
 using the routine standard methods as set forth
 in the previously mentioned Bonner and Var-
 ner text.

It will be seen that many of the phosphonic
 acid derivatives used in the practice of the

present invention conform to the general formula:



wherein: one of x and y is 0 and the other is 0 or 1;

R^9 represents haloethyl or phosphonethyl;

R^{10} represents a hydrogen atom or a substituted or unsubstituted phenyl group; and

R^{11} represents a hydrogen atom, a substituted or unsubstituted phenyl group, or a halogen-substituted or unsubstituted, saturated or unsaturated hydrocarbon chain containing from 2 to 12 carbon atoms.

It can be seen that the alkyl diesters have been excluded from the scope of the phosphonic acid derivatives usable in the method of the present invention. Such alkyl diesters have not shown any significant latex stimulating results. However, aryl diesters, or even mixed alkyl and aryl diesters and cyclic esters, have proved to be effective, and are thus included.

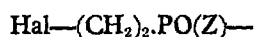
In the definition given hereinbefore for the substituent R it is stated that R can represent a phosphonoethyl group. Such a group is preferably of the general formula



wherein:

Y is a chlorine atom or an $-\text{OR}^{12}$ group;

R^{12} is a hydrogen atom, a salt-forming cation, or a substituted or unsubstituted aryl, arylmethylene, heterocyclyl or heterocyclylmethylene group, or is the



group;

Hal is a halogen atom; and either Z is defined as (but not necessarily identical to) Y , or

Z is an oxyhydrocarbon group wherein the hydrocarbon claim may be substituted or unsubstituted, saturated or unsaturated; or

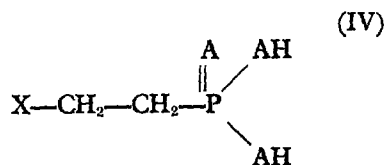
Z and R^{12} together form an $-\text{O}-\text{O}-$, $-\text{O}-\text{CH}_2-\text{O}-$, $-\text{O}-\text{CO}-\text{O}-$ or $-\text{NH}-\text{CO}-\text{O}-$ linkage, where O represents a divalent, substituted or unsubstituted benzene or heterocyclic ring.

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.

The substituted or unsubstituted, saturated or unsaturated hydrocarbon chains present in the phosphonic acid derivatives usable in the practice of the present invention will normally be lower alkyl or cycloalkyl groups, such as ethyl, isopropyl, butyl, and cyclohexyl groups. The hydrocarbon grouping

preferably contains not more than 18 carbon atoms, since above 18 carbon atoms it has been found that the water-solubility of the compounds decreases undesirably.

Another group of preferred phosphonic acid derivatives that falls within general formula I is that having the general formula:



(wherein: X represents a halogen atom or a phosphono group $-\text{PO}(\text{Y})\text{Z}$ as hereinbefore defined; and A is as defined hereinbefore) and their acid chlorides, amides, and half, full and cyclic esters. Within this group fall the phosphonothionic acid derivatives, the phosphonotriithioic acid derivatives, and the phosphonodithioic acid derivatives.

It has been determined that a positive reaction in a tomato epinasty test is a reliable indicator of an ethylene or ethylene-type response. Each named compound within the scope of the present invention has shown a positive tomato epinasty response, and such a response has been confirmed with an increase in latex flow in rubber (*Hevea brasiliensis*).

The phosphonic acid derivatives employed in the present invention may be prepared by using conventional techniques—for example, those described in United States of America Patent Specifications Nos. 3,531,549 and 3,551,528.

The catechol cyclic esters employed as a starting material for producing some of the compounds used in the method of the invention may be prepared in accordance with the process disclosed in Kabachnik *et al*, Izvest, Akad Nauk SSSP, o.k.h.n. 1947, 97 (Chem. Abstracts 42, 4132e). Thus, as disclosed by Kabachnik *et al*, these catechol cyclic esters are produced by reacting a 2-haloethylphosphonyl chloride with catechol or a substituted catechol. For example, 2-chloroethylphosphonyl chloride is heated with catechol at $150^\circ-160^\circ\text{C}$. to produce the catechol cyclic ester of 2-chloroethylphosphonic acid. Similarly, a substituted catechol (for example, a halo catechol), produced by adding chlorine or bromine to an acetic acid solution of catechol, may be reacted with 2-chloroethylphosphonyl chloride to produce the corresponding cyclic ester. As a further alternative, the catechol cyclic ester of 2-chloroethylphosphonic acid may be treated to effect substitution thereof. Thus, for example, an *o*-dichlorobenzene solution of the catechol cyclic ester of 2-chloroethylphosphonic acid may be warmed with an excess of sulphonyl chloride to produce a tetrachloro substituted catechol cyclic ester of 2-chloroethylphosphonic acid.

The following Examples and Test Results are now given, though only by way of illustration, to show details of preparative processes and compositions relevant to this invention.

5 *Example 1 — 2-bromoethyl-phosphonic acid*
Stage A: 2-bromoethyl-phosphonic acid
diethyl ester.

The diethyl ester was synthesized following the procedure of Garner, Chapin & Scanlon,
 10 "J. Org. Chem." 24, 532 (1959).

1501 g (8.0 moles) of ethylene dibromide were heated to reflux at 131°C, and 366 g (2.2 moles) of freshly distilled triethyl phosphite (B.P. 156—7°C) were added dropwise
 15 over a period of three hours. During the addition of the phosphite and subsequent heating of the mixture to a final temperature of 145°C over a period of 4 hours, 224 g (2.05 moles) of ethyl bromide were distilled from the reaction mixture.

After stripping off excess ethylene dibromide, the residue was vacuum distilled through an eight inch Vigreux column. A main fraction of 343 g ($n_D^{24} 1.4566$; b.p. 86°—88°C at 1 mm) was collected. This was redistilled through a bubble column fitted with a variable reflux distilling head, and a main fraction of 277 g of the diethyl ester of 2-bromoethyl - phosphonic acid, having
 20 $n_D^{24} 1.4579$, was collected.

Stage B: 2-bromoethyl-phosphonic acid.

Hydrolysis of the diethyl ester followed the procedure of Baer & Basu, "Can. J. Biochem". 1968, 46, 351.

277 g (1.13 mole) of diethyl 2-bromoethyl-phosphonate in 1 litre of 48% hydrobromic acid were stirred and heated in an oil bath at 95—100°C for 24 hours. The effluent gases were trapped in a cold bath to condense the ethyl bromide. Excess hydrobromic acid was removed by vacuum distillation from an oil bath at not over 60°C. The residue, upon cooling, set to a solid with a slightly yellowish cast. This was repeatedly extracted with boiling chloroform, from which 2-bromoethyl-phosphonic acid crystallized in a pure white form. M.p. 92°—94°C. Yield, 114.3 g (53%).

Example 2 — Chloroethyl-phosphondi-
(N,N-diethyl) amide.

A solution of 32.2 g (5.44 mole) of diethylamine in 100 ml of benzene was dripped into a stirred solution of 2-chloroethyl-phosphonic dichloride in 150 ml of benzene over a period of 1 3/4 hours. The resultant gel-like dispersion was stirred for two hours at room tem-
 55

perature, and after standing overnight the solid was filtered and washed with benzene. The combined filtrates were concentrated under reduced pressure to leave a residue of 25.0 g of 2-chloroethyl-phosphondi-(N,N-diethyl) amide as a clear brown viscous liquid (this represents a nearly quantitative yield).

Example 3 — 2-chloroethyl-phosphondiamide

Ammonia gas was bubbled into a solution of 183 g (1.0 mole) of 2-chloroethyl-phosphonic dichloride in 1 litre of dry benzene. After 75 g of ammonia had been added (and no more precipitate was being formed), the precipitate was filtered off, and washed with benzene. After recrystallization to remove ammonium chloride, the purified product was heated at 1 mm pressure to give a residue of 153 g of 2-chloroethyl-phosphondiamide as a viscous brown liquid.

Example 4 — 2-chloroethyl-thiophosphonic acid di-isopropyl ester.

After washing with nitrogen, 150 g of vinyl chloride was introduced, over a period of 90 minutes and at 156°—162°C while vigorously stirring, into a mixture of 710 g di-isopropylthiophosphite and 6 g di-*t*-butyl peroxide. The excess of thiophosphite was vacuum distilled off with an aspirator, and high vacuum distillation at 78°C—83°C at a pressure of 0.5 mm mercury gave 585 g of 2-chloroethyl-thiophosphonic acid di-isopropyl ester (which corresponds to a yield of 61.5% based on the used dialkyl thiophosphite, and of 100% based on the used vinyl chloride).

Test Results.

Test No. 1.

The effectiveness of 2-bromoethyl-phosphonic acid and 2-chloroethyl-phosphonic acid diamide was determined by applying each compound as a 10% mixture with palm oil. Each application was made at a rate of 3 mls per tree (0.3 gms acid equivalent per tree). Tapping was S/2 d/2.

For the bromo compound the average yield was 2,399 mls per tapping, and with the diamide the average yield per tapping was 1,988 mls. A control gave 1,125 mls. Thus, there was a 107% increase in latex flow for the bromo compound, and a 98% increase for the diamine (the control being 0%).

The pertinent data for the foregoing test, including the daily reading, as set forth in the following Table A:

TABLE A

Collection Date	Bromo	Diamide	Control
Yield Prior to Treatment (mls)	1159	1004	1120
October 15	4105	3765	995
October 17	3020	2210	1005
October 21	2630	2360	1090
October 23	2395	1715	1015
October 26	3225	2680	1020
October 28	2170	1720	830
October 30	2420	1785	830
November 6	2110	1880	950
November 13	1680	1665	1005
November 20	2280	2085	1760
November 24	2020	1905	1510
December 4	1775	1660	1125
(Retreatment on December 8)			
December 10	1930	1695	1205
December 18	4060	3972	1075
December 24	2655	2291	1115
December 28	1820	1540	955
January 11	2008	1745	1127
January 13	2160	1970	1357
January 15	1890	1495	1070
January 19	1950	1628	865
January 21	2132	1665	1102
January 25	2195	1597	1115
January 29	2435	1957	1282
February 2	2066	1825	940
February 4	1870	1875	1235
February 6	2160	1760	1110
February 8	2095	1790	1190
February 10	2367	1770	1350
February 12	2195	1830	1190
February 16	1956	1465	1037
February 18	1976	1620	1158
(Retreatment on February 18)			
February 20	4757	2765	1205
February 22	3470	3030	1130
February 24	1930	1425	1005
February 26	1040	1445	1070

The active ingredient in the palm oil formulation was applied to a scraped bark approximately 1 1/2" below the tapping cut.

- 5 For the control, treatment consisted of applying palm oil only.
Test No. 2.

- 10 Another test was run to show the effectiveness of 2-chloroethyl-phosphonic acid diamide. The active ingredient was present in a proportion of 10% by weight. The formulation was applied to scraped bark below the tapping cut, and all treatments were applied at a rate of 3 mls per tree (0.3 gms acid equivalent per

tree). The diamide showed an overall latex yield of 233% as compared with the control (which was 105%)—thus a 128% increase. With respect to the diamide species, the yield prior to treatment was an average of 581 mls per tree whereas after treatment the yield was 1356 mls per tap. Similar figures for the control were 825 mls (per treatment) and 872 mls.

The control was an application of pure palm oil alone.

The foregoing results are based on the data set forth in Table B below.

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TABLE B.
Pre-treatment data.

	Date	Yield—mls
	November 11	560
5	November 23	710
	October 12	600
	December 23	543
	December 26	580
	January 11	495
10		Average = 581

Post-treatment data.

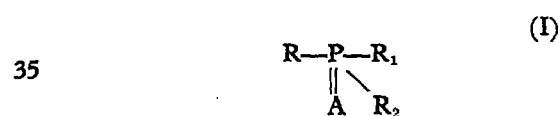
	Date	Yield—mls
	January 14	523
	January 17	1575
15	January 20	1835
	January 23	1920
	February 5	1715
	February 8	1095
		Average = 1443

20	February 11	1250
	February 14	1190
	February 18	1190
	February 21	1420
	February 25	1335
25	February 28	1235
		Average = 1270

No claim is made to the use of the compound 2-chloroethylphosphonic acid. Subject to this disclaimer,

30 WHAT WE CLAIM IS:—

1. A method for the stimulation of latex flow in rubber trees, in which there is applied to the tree a phosphonic acid derivative of the general formula:



wherein:

R represents either a halo-ethyl or a phosphono-ethyl group;

40 A represents an oxygen or sulphur atom; and

1) R₁ and R₂, which are same or different, each represent a chlorine atom, a hydroxy group or a mercapto group; or

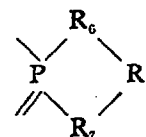
45 2) R₁ and R₂, which are same or different, are each an —AR₃ group or an —A—CH₂R₃ group, wherein A is as defined hereinabove, and each R₃, which are the same, represents a substituted or unsubstituted aryl group or a heterocyclic group; or

50 3) R₁ and R₂ which may be the same or different, are each an —AR₄ group or an —A—CH₂R₄ group (wherein A is as defined hereinabove, and the two groups R₄ are different, and each represents a hydrogen

atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a heterocyclic group, an alkene group or an alkyne group, provided that at least one R₄ group represents a hydrogen atom, a substituted or unsubstituted aryl group, or a heterocyclic group); or

60 4) One of R₁ and R₂ is an —AR₅ group and the other is an —A.P(=A)(AR₅)R group (wherein A is as defined hereinabove, and each R₅ group, which may be the same or different, represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a heterocyclic group, and wherein R is as defined hereinbefore); or

70 5) R₁ and R₂, together with the phosphorus atom, represent the cyclic group



(wherein one of R₆ and R₇ is —A— and the other is —A—, —CA—A— or —CA—NH—, A is as defined hereinabove, and R₈ represents a divalent phenylene or substituted or unsubstituted heterocyclic ring), or a salt, amide or anhydride of any appropriate such phosphonic acid derivative.

2. A method as claimed in claim 1, in which the compound employed has a substituent R which is the 2-bromoethyl or 2-iodoethyl group.

3. A method as claimed in either of the preceding claims, in which the compound employed is:

85 a 2-chloroethyl mono-ester or a *o*-hydroxyphenyl mono-ester;
a diphenyl diester or a *bis*-(2-oxo-1-pyrrolidinyl)methyl diester;
a mixed 2-hydroxyphenyl/alkyl, alkenyl or aryl ester; or

90 a pyrocatechol, 4-chloropyrocatechol, tetrachloropyrocatechol, salicyclic acid, saligenin or 2,3-pyridinediol cyclic ester.

4. A method as claimed in either of claims 1 and 2, in which the compound employed is an acid chloride.

5. A method as claimed in any of the preceding claims, in which the compound employed is such that all the substituents A are oxygen atoms.

6. A method as claimed in claim 1, in which the compound employed is a haloethyl phosphonic acid derivative of the general formula:

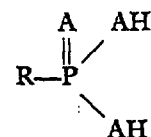




TABLE B.
Pre-treatment data.

	Date	Yield—mls
	November 11	560
5	November 23	710
	October 12	600
	December 23	543
	December 26	580
	January 11	495

10 Average = 581

	Date	Yield—mls
	January 14	523
	January 17	1575
15	January 20	1835
	January 23	1920
	February 5	1715
	February 8	1095

Average = 1443

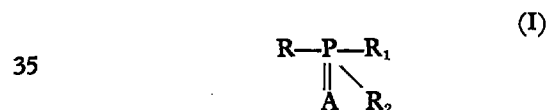
20	February 11	1250
	February 14	1190
	February 18	1190
	February 21	1420
	February 25	1335
25	February 28	1235

Average = 1270

No claim is made to the use of the compound 2-chloroethylphosphonic acid. Subject to this disclaimer,

30 WHAT WE CLAIM IS:—

1. A method for the stimulation of latex flow in rubber trees, in which there is applied to the tree a phosphonic acid derivative of the general formula:



wherein:

R represents either a halo-ethyl or a phosphono-ethyl group;

40 A represents an oxygen or sulphur atom; and

1) R₁ and R₂, which are same or different, each represent a chlorine atom, a hydroxy group or a mercapto group; or

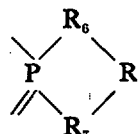
45 2) R₁ and R₂, which are same or different, are each an —AR₃ group or an —A—CH₂R₃ group, wherein A is as defined hereinabove, and each R₃, which are the same, represents a substituted or unsubstituted aryl group or a heterocyclic group; or

50 3) R₁ and R₂ which may be the same or different, are each an —AR₄ group or an —A—CH₂R₄ group (wherein A is as defined hereinabove, and the two groups R₄ are different, and each represents a hydrogen

atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a heterocyclic group, an alkene group or an alkyne group, provided that at least one R₄ group represents a hydrogen atom, a substituted or unsubstituted aryl group, or a heterocyclic group); or

60 4) One of R₁ and R₂ is an —AR₅ group and the other is an —A.P(=A)(AR₅).R group (wherein A is as defined hereinabove, and each R₅ group, which may be the same or different, represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a heterocyclic group, and wherein R is as defined hereinbefore); or

70 5) R₁ and R₂, together with the phosphorus atom, represent the cyclic group



(wherein one of R₆ and R₇ is —A— and the other is —A—, —CA—A— or —CA—NH—, A is as defined hereinabove, and R₈ represents a divalent phenylene or substituted or unsubstituted heterocyclic ring), or a salt, amide or anhydride of any appropriate such phosphonic acid derivative.

2. A method as claimed in claim 1, in which the compound employed has a substituent R which is the 2-bromoethyl or 2-iodoethyl group.

3. A method as claimed in either of the preceding claims, in which the compound employed is:

85 a 2-chloroethyl mono-ester or a *o*-hydroxyphenyl mono-ester;

90 a diphenyl diester or a *bis*-(2-oxo-1-pyrrolidinyl)methyl diester;

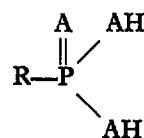
a mixed 2-hydroxyphenyl/alkyl, alkenyl or aryl ester; or

95 a pyrocatechol, 4-chloropyrocatechol, tetrachloropyrocatechol, salicylic acid, saligenin or 2,3-pyridinediol cyclic ester.

4. A method as claimed in either of claims 1 and 2, in which the compound employed is an acid chloride.

5. A method as claimed in any of the preceding claims, in which the compound employed is such that all the substituents A are oxygen atoms.

6. A method as claimed in claim 1, in which the compound employed is a haloethyl phosphonic acid derivative of the general formula:





- (wherein R and A are as defined in claim 1, and at least one A substituent is a sulphur atom).
7. A method as claimed in claim 1, in which the compound employed is:
- 5 2-chloroethylphosphonic acid diamide;
N,N¹-dimethyl 2-chloroethylphosphonic acid diamide; and
N,N,N¹,N¹-tetramethyl 2-chloroethylphosphonic acid diamide.
- 10 8. A method as claimed in claim 1, in which the compound employed is:
- the *bis*(acid chloride) or 2-chloroethyl-phosphonic acid;
- 15 the pyrocatechol cyclic ester of 2-chloroethylphosphonic acid;
- the 4-chloropyrocatechol cyclic ester of 2-ethylphosphonic acid;
- 20 the mixed ethyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- the mixed butyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- 25 the mixed propynyl and 2-hydroxyphenyl di-ester of 2-chloroethylphosphonic acid;
- the 2-chloroethyl monoester of 2-chloroethyl phosphonic acid;
- 2-bromoethylphosphonic acid;
- 30 the *bis*(phenyl)-ester of 2-chloroethylphosphonic acid;
- the tetrachloropyrocatechol cyclic ester of 2-chloroethylphosphonic acid;
- 2-iodoethylphosphonic acid;
- 35 the saligenin cyclic ester of 2-chloroethylphosphonic acid;
- the salicylic acid cyclic ester of 2-chloroethylphosphonic acid;
- phosphonoethyl phosphonic acid;
- phosphonoethylthioethylphosphonic acid;
- 40 the 3-hydroxyphenyl monoester of 2-chloroethylphosphonic acid (which exists in polymeric form);
- the *bis*(2-oxo-pyrrolidinylmethyl) ester of 2-chloroethylphosphonic acid;
- 45 the *o*-hydroxyphenyl monoester of 2-chloroethylphosphonic acid;
- the mixed isopropyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- 2-fluoroethylphosphonic acid;
- the mixed octyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- 50 the mixed hexadecyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- the mixed tridecyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- 55 2-chloroethylphosphonic anhydride;
- 2-chloroethylbutylester, 2-hydroxyphenyl-ester of phosphonic acid;
- 2-chloroethyl-2-chloroethyl ester of phosphonic acid; or
- 60 2-chloroethyl-phosphonothionic acid, -phosphonotrithioic acid or -phosphonodithioic acid.
9. A method as claimed in claim 1, in which the compound employed is:
- 65 the salicylic acid cyclic ester of 2-chloroethyl-phosphonoamidic acid;
- the mixed phenyl and 2-hydroxyphenyl diester of 2-chloroethylphosphonic acid;
- 2-chloroethyl-dichloro-phosphine;
- 70 the *bis*(pentachlorophenyl) ester of 2-chloroethyl-phosphonic acid;
- the 2,3-pyridinediol cyclic ester of 2-chloroethylphosphonic acid;
- 2-chloroethyl-thiophosphonic acid (or its 2-bromo-, 2-fluoro- and 2-iodo analogues);
- 75 or
- the 2-chloroethyl-2,3-dibromo-4-hydroxy-2-butenyl phosphonic acid ester polymer.
10. A method as claimed in claim 1, in which the compound employed is a sodium, 80 aluminium, zinc, potassium or lithium salt.
11. A method as claimed in any of the preceding claims, in which the phosphonic acid derivative is applied to the tree as an aqueous solution thereof. 85
12. A method as claimed in any of the preceding claims in which there is applied at least 0.30 gms. (free acid equivalent) per tree of the phosphonic acid derivative.
13. A method as claimed in any of the preceding claims and substantially as described 90 hereinbefore, especially with reference to the Test Results.
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