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PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE RIPENING OF TOBACCO

(71) We, AMCHEM PRODUCTS, INC., a Corporation organized 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 concerns improvements in or relating to the ripening of tobacco. More particularly it relates to methods for accelerating or otherwise controlling tobacco ripening, the term "ripening" being used to mean the biochemical and physical changes in the tobacco leaf, both before and after harvesting thereof, which render it marketable as regards colour, texture and aroma.

Tobacco is an economically-important crop which is grown worldwide — very often under adverse conditions of soil and climate. The ripened and dried leaves of the tobacco plant are rolled to make cigars or shredded to make cigarettes. There are several different varieties of the tobacco plant, *Nicotiana tabacum*, but for the purposes of this invention they can all be regarded as essentially the same. The fully-grown tobacco plant stands about four to five feet high (say 120—150 cms); and its leaves vary in size — being about one to two feet long (say 30—60 cms) near the base of the stem, but only about three or four inches long (say 7.5—10 cms) near the top of the stem. During growth the leaves are darkish-green in colour; but as the plant reaches maturity the leaves change in colour. First the darkish-green leaves become mottled in colour and begin to pucker, then the leaves become a lighter-green colour (indicating that they are now fully developed and physiologically-mature) and finally they develop patches of yellow, which spread until each leaf is a light-yellow colour all over. This colour change — which indicates "ripening" — begins with the most mature leaves (at the base of the plant-stem or stalk) and moves upwardly to finish with

the least mature leaves (at the top of the plant-stem or stalk). When any leaf is fully yellow it is then ripe, and is in an ideal condition for harvesting, drying and using. 50

The ripening of even a single leaf, signalled by its change in colour, may take several weeks under natural conditions; and the ripening of all the leaves on any one plant always takes still longer, because the upper leaves may not start to change colour until the lower leaves have finished their colour-change. It is however possible for a tobacco leaf to ripen after it has been picked, or after the whole plant has been cut down. Generally-speaking, there are two different methods of harvesting tobacco, called respectively the "stalk-cutting" system and the "priming" system, which are as follows: 55 60 65

(a) Stalk-cutting System

In this harvesting method one cuts down the whole plant, by cutting its stalk near the base thereof, usually at the stage when the lowermost three or four leaves have ripened (turned yellow) substantially completely. The aim is to harvest the entire crop by stalk-cutting at one time, though naturally it may sometimes be necessary to cut selectively. After cutting the whole plants are hung on laths, and the laths are placed on racks in a curing barn. The other leaves ripen in the barn, even if they were not fully-developed when the stalk was cut. 70 75

(b) Priming System

In this harvesting method one picks the leaves individually from the stalk at intervals, more or less as each one becomes fully-developed and starts ripening. Thus in the priming system the tobacco crop is gathered selectively part by part, on a number of different occasions. At each gathering only those leaves are picked that show signs of ripening, that is to say those which are in the best ("prime") condition for harvesting. Each gathering is therefore commonly called a "priming", from which the system gets its 80 85 90

name. The harvest commences when at least one of the lowermost leaves, and usually three or four of them, have reached commercial size, and show signs of ripening. These fully-developed and ripening leaves are gathered in the so-called first "priming"; and that is followed by a succession of four or five subsequent gathering or "primings", of from two to four more leaves each time, at intervals between successive gatherings of about 5 to 10 days. The picked leaves are then strung on sticks, where they complete their ripening (if necessary) and are allowed to air-dry before being cured by any desired curing process.

Like most crops, tobacco has a growing season; if it is planted at the correct time at the beginning of its growing season, then the tobacco will reach a harvesting stage near the end of its growing-season. As with most crops, the actual period from planting to harvesting varies — but with tobacco the variation from plant to plant and from field to field is greater than with most other crops, and it is markedly dependent on the weather. Therefore it is not only impossible to predict accurately when a tobacco crop will be ready for harvesting, but it is even impossible to expect all the tobacco plants in one particular crop to reach the harvesting stage at the same time. The actual gathering of the harvest of the ripening tobacco leaves can be done by machine, but quite often it is still done by hand. Less damage to the leaves is caused by hand-picking than by machine-picking, and a human hand-picker can more easily distinguish between leaves which are ready for picking and leaves which are not. Irrespective of whether the harvest is gathered by hand or by machine, it is an inconvenient and costly fact that not all the leaves on any one plant ripen at the same time, since this forces the tobacco-farmer either to harvest the entire crop by stalk-cutting perhaps before all the leaves are fully-developed or to gather in only part of the crop by priming on a number of different occasions. The first alternative is wasteful of tobacco and the second is wasteful of labour.

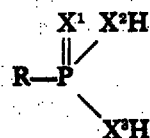
The stalk-cutting system of harvesting tobacco is less labour-intensive than the priming system, at least during harvesting, and indeed most tobacco is harvested by the stalk-cutting system unless it is to be flue-cured. Despite the lower labour-costs of the stalk-cutting system, there are however distinct advantages to the priming system of harvesting tobacco. The successive harvesting of the lower leaves causes the remaining, upper leaves to gain in weight; and the detachment of the leaves from the stalk prevents any weight loss which otherwise would occur due to translocation of water, minerals, sugars *etcetera* from the leaf to the stalk during curing. For these reasons the weight of tobacco leaves harvested by the priming system tends to be on average 20%—25% greater than the weight

of tobacco leaves harvested by the stalk-cutting system. The quality of the tobacco also tends to be better, since each leaf is harvested in "prime" condition, and because hand-picking (which is usually employed) helps to avoid damage to the leaves.

We have now found that most of the advantages of the priming system of harvesting tobacco can be secured with fewer primings and thus lower costs if the ripening of the leaves is accelerated by treating the tobacco plants, at a very late stage in their growth, with an effective amount of certain phosphonic acid (or thio-phosphonic acid) derivatives.

According to one aspect of the invention there is provided a process for accelerating the ripening of tobacco leaves, preparatory to their harvesting and curing, in which to the leaf, when it is fully-developed and has reached physiological-maturity, there is applied while the leaf is still fresh an effective amount, not exceeding 200 milligrams per tobacco plant, of one or more phosphonic acid compounds which conform to general formula

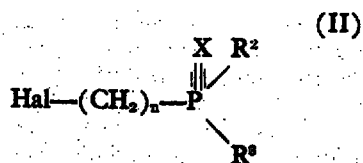
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(where X^1 , X^2 and X^3 , which may be the same or different, are each oxygen or sulphur; and R is an alkyl or alkenyl group, optionally substituted by one or more hydroxy, alkoxy, amino, substituted amino or quaternized amino, halo, cyano, carboxyl, sulphonamido or phosphono groups) or corresponding functional derivatives thereof being salts, hydrolyzable esters, amides acid halides or anhydrides formed with the $-\text{X}^2\text{H}$ and/or $-\text{X}^3\text{H}$ groups of the phosphonic acid compounds of general formula I above.

It will be understood that the just-mentioned functional derivatives corresponding to the phosphonic acid compounds of general formula I above include monosubstituted derivatives of the acid function and also disubstituted derivatives thereof, the latter being derivatives either of the same kind or different. Thus for instance the functional derivatives can be mono- or di-salts, mono- or di-esters, mono- or di-amides, mono- or di-halides, or either internal or external anhydrides, and they can in addition be mixed salt/esters, ester/amides and so on. Moreover the functional derivatives can be cyclic, for instance cyclic esters, cyclic amides, cyclic ester/amides and so on. Furthermore, the amides may be either N-substituted or unsubstituted.

The phosphonic acid compounds of general formula I and functional derivatives thereof used in the process of this invention will very preferably be one or more of those conforming to the general formula



wherein:

X represents oxygen or sulphur;

n is an integer from 1 to 6;

Hal represents a halogen atom; and

R² and R³ both represent either hydroxy groups or amino groups, or one of them represents a hydroxy group while the other represents an alkoxy or substituted-alkoxy group, or R² and R³ together represent the residue of an anhydride.

The phosphonic acid compounds of general formula I and their functional derivatives which are most preferred for use in the process of this invention, because far more development work has been carried out upon them than upon the others, are those of general formula II above wherein X represents oxygen and n is 2, namely 2-halo-ethyl phosphonic acids and the salts, hydrolyzable esters and amides thereof.

The specific preferred phosphonic acid compound for use in the process of this invention is the free acid wherein Hal represents chlorine, namely 2-chloroethyl phosphonic acid (commonly known as "ethephon"), whose effect is typical of all such compounds and functional derivatives thereof and is used to illustrate the invention hereinafter. Other suitable derivatives thereof, which give the typical response when applied to tobacco, are as follows:—

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 tetrachloropyrocatechol 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 2-hydroxyphenyl monoester of 2-chloroethyl phosphonic acid (in polymer form);

the bis-(2-oxo-pyrrolidinyl-methyl) diester of 2-chloroethyl-phosphonic acid;

the mixed phenyl and O-hydroxyphenyl diester of 2-chloroethyl phosphonic acid;

the O-hydroxyphenyl monoester of 2-chloroethyl-phosphonic acid;

the mixed isopropyl and 2-hydroxy-phenyl diester of 2-chloroethyl-phosphonic acid;

the mixed octyl and 2-hydroxyphenyl 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.

The specific derivatives identified above represent those which for practical reasons it is preferred to employ, but in order to illustrate the scope of the invention it may be mentioned that the following other compounds and derivatives can be employed equally successfully, namely:—

2-bromoethyl-phosphonic acid, and its derivatives corresponding to those listed above for ethephon;

2-iodoethyl-phosphonic acid, and its derivatives corresponding to those listed above for ethephon;

2-fluoroethyl-phosphonic acid, and its derivatives corresponding to those listed above for ethephon; and

phosphono-ethyl phosphonic acid, and its derivatives corresponding to those listed above for ethephon.

Still further compounds which have been shown to be active, though not necessarily of equal activity, are as follows:—

allyl-phosphonic acid;

vinyl-phosphonic acid;

2,3-dichloropropyl-phosphonic acid;

2-methoxyethyl-phosphonic acid;

carboxymethyl-phosphonic acid; and

2-chloropropyl-phosphonic acid

as well as their derivatives corresponding to those listed above for ethephon — such as for instance the pyrocatechol cyclic ester of vinyl phosphonic acid.

The application of the phosphonic acid compound of general formula I or derivative thereof will not be effective if it takes place before the leaf is fully-developed. The application must also take place while the leaf is fresh — which nearly always means while the leaf is on the growing plant, but in an extreme and unusual case includes application immediately after the leaf has been picked or the stalk cut, before any wilting has occurred and

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thus while the leaf is still sufficiently alive to permit translocation of the phosphonic acid compound or derivative thereof into its system.

5 In its broadest aspect the invention envisages application to a single leaf — but for most practical purposes application must take place by spraying at least one whole plant at a time, and indeed usually an entire field in a single operation.

10 It is thus a greatly-preferred feature of this invention to provide a process for accelerating the ripening of tobacco leaves, as herein disclosed, in which an effective amount of one or more of the phosphonic acid compound(s) of general formula I and/or the aforesaid functional derivatives thereof is applied to the plant only after substantially all the leaves are fully-developed and have reached physiological maturity and while the leaves are still fresh.

20 Although it may sometimes be possible to defer any harvesting operation until after application of the phosphonic acid compound(s) and/or derivatives, this entails some danger that the lowermost leaves on the plant may become over-ripe before they are gathered. Mostly therefore it will be advantageous to gather the fully-developed lower leaves, prior to the application, by the priming system. In general it will then be found that application should take place after the second priming.

35 The leaves may be harvested immediately before the phosphonic compound(s) and/or functional derivative(s) thereof have been applied thereto, provided the leaf — or the plant, as the case may be — is still fresh and unwilted. Normally however they will be harvested up to 4 days after application since ripening will continue in the barn. The method of harvesting then employed may be either the priming system or the stalk-cutting system. Since the application accelerates the ripening of the fully-developed leaves irrespective of whether they remain upon the growing plant or not, there is an advantage whichever system is employed. If the remainder of the harvest is gathered by the stalk-cutting system, the ripening period in the barn is reduced; while if it is gathered by the priming system, the number and spacing of subsequent primings will be thereby reduced as compared with untreated plants.

50 In the process of this invention it is necessary that an "effective amount" of the phosphonic acid compound(s) and/or derivative(s) should be applied to the fresh leaves, usually while they are still on the growing plant. For reasons of economy, the amount applied should be near the minimum, but it is not possible to specify the minimum effective amount with complete precision, since it can vary somewhat dependent on the variety of tobacco being treated, and its stage growth, as well as the prevailing climatic and soil conditions, and indeed the actual compound being employed

and the manner in which it is applied. For general guidance it can however be noted that in practice more than 200 milligrams per plant is not required, and that normally from 50 to 150 milligrams of the phosphonic acid per plant will suffice. The optimum rate of application can be determined by simple trials — if the rate is too high, the leaves will be scorched; while if the rate is too low, the ripening effect will be uneven.

Although the application rates indicated above are given in terms of milligrams per plant, they can and normally will be established in terms of weight per unit area of the field containing the tobacco crop. Normally the recommended field-application rate will be around 2 pounds per acre dissolved in 40—50 United States gallons (approximately equivalent to 2.2 kilograms per hectare, dissolved in about 370—460 litres) of water. The population of tobacco plants in a crop is usually in the range of from 5,000 to 9,800 plants per acre (or approximately from 12,350 to 24,200 plants per hectare) and thus the recommended application rate corresponds approximately to 100 milligrams per plant. Variations in plant-density are roughly self-compensating, since as plant-density increases so plant-size decreases, and *vice versa*. There must obviously be some wastage of the sprayed material upon the group, but this is not a critical factor.

The phosphonic acid compound(s) of general formula I and/or functional derivatives thereof may be applied to the tobacco either in pure form or in impure ("technical grade") form — but they can be applied much more conveniently in the form of compositions wherein they are mixed with suitable carriers for use in agricultural compositions. Although other carriers or vehicles can be employed, such as pulverulent solid vehicles and non-aqueous liquid vehicles, the most suitable vehicle appears to be water, and preferably water containing an acid or a buffering agent to keep the composition of an acid pH of 5 or less, so as to prevent or reduce unwanted hydrolysis of the phosphonic acid compound(s).

Most ready-for-use compositions will be fairly dilute, ranging normally between 0.04 and 0.4 pounds per U.S. gallon (about 4.8 to 48 grams per litre) of the phosphonic acid compound(s) and/or derivatives — and, as previously indicated, the usually-recommended use-concentration is about 0.04 pounds per U.S. gallon (about 0.48 grams per litre).

For storage and distribution it is however desirable to have a concentrate, which can in an extreme case contain as much as 95% by weight of the phosphonic acid compound(s) of general formula I and/or functional derivatives thereof, and in practice will seldom contain less than 30% by weight. The preferred concentrates are those containing 40%—60%, and the recommended concentrate will contain

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about 4 pounds of the phosphonic acid compound(s) and/or derivatives per U.S. gallon (about 0.48 kg per litre).

As already indicated, the preferred phosphonic acid compound for use in the process of the invention is ethephon, i.e. 2-chloroethyl phosphonic acid. The preferred compositions therefore consist essentially of an aqueous solution of ethephon, which however may be the impure "technical grade" material — which as currently available on the market contains about 87.3% by weight of ethephon, the balance being mainly various phosphonic acids such as unsaturated poly-phosphonic acid and ethane diphosphonic acid.

Aqueous solutions of ethephon and functional derivatives thereof are liable to undergo hydrolytic breakdown (with consequent loss of activity) releasing ethylene gas which is liable to catch fire. The compositions therefore will very desirably also contain one or more stabilizers, designed to prevent or at least minimize such hydrolytic breakdown in the concentrates. The hydrolytic breakdown occurs only very little at acid pH values of 5 or less. Consequently the compositions will advantageously include one or more acids and/or buffers, such that the pH of the concentrate is not greater than 5, to serve as stabilizer. It has also been found that "anti-freeze" compounds, such as polyethylene glycol, serve as stabilizers. Even in the presence of such stabilizers there remains a danger of some hydrolytic breakdown, and consequently it is strongly recommended that the concentrates should be packaged within a stoppered, non-frangible, pressure-resistant container formed of chemically-inert material.

After the tobacco leaves have been harvested they must be dried and cured. There are numerous different methods of curing the harvested tobacco — such as those known as field curing, air curing, flue curing and fire curing — and some varieties of tobacco are more suited to being cured by one method than another. The ripening/drying/curing of a tobacco leaf involves many complicated physiological changes — but it is sufficient for the purposes of the present invention to say that, broadly-speaking the drying and curing of tobacco is carried out simply by keeping the picked leaves in a warm, dry environment until each leaf not only has ripened fully (turning a light yellow) but also has dried, losing most (but not all) of its moisture content. The faster the ripening/drying/curing takes place, either in the field or the curing barn or curing oven, the better the use that can be made of the field-space and/or the barn- or oven-space which is available.

It will therefore be appreciated that the process of this invention can have far-reaching beneficial effects on tobacco cultivation and harvesting. It enables the ripening and harvesting of tobacco to be initiated at the de-

sired moment and completed in a predictable time, thus permitting the farmer to make the most efficient use of his harvesting labour and/or machinery and of his curing-barn and/or curing-oven capacity. Harvesting can be initiated at or about a time of optimum weather conditions, so that the effects of late-season rains or other adverse weather conditions can probably be avoided. If harvesting is carried out using the priming system, the number of primings after treatment is much reduced, thus aiding the efficient use of the labour force, and minimizing the damage caused each time the labour force goes through the field. By positively inducing leaf-ripening it minimizes losses due to irregular climatic conditions, uneven sun exposure and temperature variations. Very importantly, the treatment largely or even wholly prevents so-called "flush back", a phenomenon in which a green colour returns to the leaf (after it has turned yellow) if it is left on the stalk longer than usual. Moreover, by accelerating ripening the process of this invention makes it possible to complete the harvest more quickly — which sometimes may enable a second crop, such as rice, to be grown successfully in the interval between the tobacco harvest time and the onset of adverse weather conditions at the end of the growing season.

The advantages in field-harvesting described above are equalled by the advantages in curing. Firstly, the process of the invention enables the curing barns and/or curing-ovens to operate as full or near-full capacity during the expected harvest, by reducing or eliminating the partial or irregular ripening of the tobacco leaves — and the costs of both labour and fuel are thereby reduced. Secondly, by careful planning it is possible to pass the entire crop through the curing stage in a steady stream at a faster rate than normal. This can be illustrated as follows, with reference to flue-cured tobacco, for which the normal flue-curing time in the curing barn is about 7 days. However when the tobacco growing in the field is treated by the process of this invention, the leaves by the time they are gathered will reach the curing barn in a condition normally attained only after they have been kept in the barn, under flue-curing conditions, for two to three days. Consequently the leaves need be cured in the curing-barn for only about 4 days instead of 7 days. If then the farmer applies the phosphonic acid compound(s) and/or derivative(s), at 4-day intervals, each time to a section of the crop which will fill his curing-barn, he can expect to fill and empty his barn about every four days, which represents a great improvement upon existing practice.

In another aspect of this invention there is indeed provided a process of harvesting and curing a tobacco crop in which the curing-period for tobacco to which there has been applied an effective amount of one or more of

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the phosphonic acid compound(s) of general formula I and/or the aforesaid functional derivative(s) thereof is determined, and successive applications thereof are made at time-intervals substantially the same as that curing-period, each successive application being made only to a section of the crop corresponding in size to the curing-capacity available, so that each crop-section becomes ripe and ready for harvesting and curing as the previously harvested crop-section completes its curing.

The control method of this invention is applicable to all types of tobacco — such as, for example, the flue-cured tobaccos White Stem, Orinoco, Cash, Jamaica, Virginia Bright and Bonanza, and the dark air-cured or fire-cured tobaccos Burley and Maryland. At least as regards flue-cured tobacco, it has been found that the flue-cured tobacco leaves are improved in quality, particularly as regards a decrease of the flush-back phenomenon.

The invention of course extends to tobacco whenever ripened, harvested and cured using the process of this invention.

In order to illustrate the advantageous effect of the process of the invention, a series of evaluations are presented below, which are however given only for purposes of illustration:—

EXPERIMENT I. EFFECT OF VARYING CONCENTRATIONS OF ETHEPHON COMPOSITIONS ON TOBACCO RIPENING

Experiments were carried out with a typical composition of the invention. A typical technical grade ethephon was used comprising about 92% of 2-chloroethyl phosphonic acid (including small proportions of the mono-2-chloroethyl-2-chloroethyl phosphonate and 2-hydroxyethyl-phosphonate isomers as well as 1.6% of 1,2-ethane diphosphonic acid and 1.5% unsaturated polyphosphonic acid) which also contained 0.5% chlorinated polyethylene glycol and had a pH of 5. Four plots, I to IV, of about 0.5 hectare (ha) each were treated with the composition of the invention spraying by airplane at the rate of four litres of the concentrate (i.e. 4 lbs. ethephon/gallon or 480 grams/litre) diluted in water to provide 100 litres of spray per hectare (or about 1.9 kg/ha). One plot, V, of the same size was left untreated, as a control.

Each of the four plots was fertilized with different nutrient levels as shown in Table I, and the untreated plot was fertilized with a level of each nutrient that was the average of the four treated plots. Each plant load was measured before and after spraying to determine the actual amount of material applied.

TABLE I

Plots	I	II	III	IV	V
Effective Areas (Sq. m.)	5450	5310	5140	4820	5720
Ethephon Concentrate (Mg/plant)	109	105	105	109	0
Ethephon Concentrate (l/ha)	4.4	4.2	4.2	4.4	0
Total Spray Vol. (l/ha)	109	105	105	103	0
Fertilizer Levels (Kg/ha.)					
N	30	45	70	70	54
P ₂ O ₅	180	90	135	180	146
K ₂ O	120	135	200	120	144

The fields were planted with tobacco variety V—9 ("flue-cured", selection of Hicks X NC 2512 X, mosaic resistant Hicks); 19,300 plants/ha were planted.

Land site selected was in an area where the land has a history of uneven and late ripening. The leaves did not normally yellow and in the

past had to be picked for field curing.

Spraying was made after the second picking, harvesting of the leaves of the lowest two nodes.

Each plot was harvested daily, picking out all leaves that were ready for harvest; these were leaves which had a pale green to yellow

color. The following information was recorded.

1. Amount and cost of labor required for daily harvesting.

2. Separation and weighing of leaves that were damaged or "flushed back" and thus had to be left for curing in the field.

3. Grading and separation of leaves by degrees of yellowing (four to five grades) from green lime to yellow to select temperature treatment and position within the oven.

4. Time required for curing in the oven by stages (yellowing, color setting, leaf drying and stem drying).

5. Yield of cured tobacco from the oven.

6. Sampling for quality comparison and for general chemical and residue analysis.

The figure in the accompanying drawing shows the effect of concentration of the treated tobacco at different rates and the accumulated number of leaves harvested per plot of 30 plants. The data show that the composition of the invention significantly speeds up the rate of ripening of the tobacco leaves so that at any given time there are a considerably greater numbers of leaves available for harvesting. A remarkable increase of unripened leaves over the control was obtained in this period of 5 to 15 days, particularly 5 to 10 days after application.

It is to be noted also that the degree of acceleration of ripening depends within certain ranges on the rate the composition is used and is noticeable at rates of application of the actual ingredient, ethephon, as low as 20 mg/plant. A level of 10 mg/plant was obtained with 400 cc of the concentrate composition (480 grams of active ingredient/liter) per hectare for plant densities of 19,300 plants per hectare. Already with 20 mg of the chemical per plant, an increase in ripened tobacco leaves was observed. Within rates of 20 to 60 mg/plant, there was practically a linear relationship between dosage and response. Also, within the first four days, there was an increase in response for rates of application over 90 mg/plant. Thus larger doses are most beneficial for short-time (up to four days), immediate results.

In only 10 days, more than about two-thirds of the number of leaves collected in the untreated control plot over a period of 29 days were collected when 60 to 100 mg of a composition of the present invention was applied to the leaves. Ripening is thus considerably accelerated and the harvesting period materially shortened.

It is to be observed also that the total yield (number of leaves harvested) increases with increasing dosages of ethephon. At the level of 100 mg/plant of the chemical, the total number of leaves harvested was 34% higher than that from the control plot.

Thus, aerial spraying of a composition of the chemical of the invention (a concentrate of 480 g/liter of active chemical at 4 liters per hectare, in 100 liters of water) produces a remarkable increase in the proportion of tobacco leaves suitable for flue-curing when high fertility of soil conditions and others are adverse for proper ripening of the tobacco leaves. In the conditions of Experiment I, treated plots showed an increase of 40% of flue-cured leaves over the control plots.

Practically all the tobacco from treated plots was harvested within 6 to 8 days from the application of the composition; in comparison, 60% of the control plots had to be continued for a period of nearly one month. The composition of the invention is especially well suited for modulated harvest timing, thus harvesting to fit oven curing programs or to avoid damaging rains on late season's harvest.

The invention makes it possible to concentrate the harvest timing within a specific period to fit oven programs. Faster ripening also results in less numerous pickings, therefore increasing the efficiency of harvesting. This allows for significant financial saving. The promotion of yellowing of tobacco leaves treated with the composition of the invention reduced by 18 hours the time required for oven curing. This in effect augments the curing capacity of oven barns and produces a direct economy of fuel, labor and supervision costs.

Aerial spray volume of about 100 liters/hectare proved quite satisfactory. When terrestrial application with manual knapsack sprayers, or even with motorized knapsack mist blowers are desired, about 500 to about 750 liters of spray volume/hectare are usually preferred for best results.

EXPERIMENT II.

In a manner similar to the procedure employed in Experiment I, a series of 25 plots, 30 plants each (corresponding to a plant density of 19,300 plants/ha), received different levels of treatment with an ethephon composition of this invention, using a knapsack manual sprayer, leaving intermediate separating plots and lateral check plots, as shown in Table II.

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TABLE II.

Plot	Mg/Plant	Liters of Spray/Hectare
1	0	0
2	60	450
3	0	0
4	79	750
5	0	0
6	54	810
7	0	0
8	60	450
9	0	0
10	79	750
11	0	0
12	54	810
13	0	0
14	100	770
15	60	450
16	0	0
17	79	750
18	0	0
19	54	810
20	0	0
21	102	770
22	102	770
23	102	770
24	0	0
25	0	0

TABLE III

Plot Number	Ethephon mg/plant	Number of Mature Leaves Harvested Per Day															
		1st Day		2nd Day		4th Day		7th Day		10th Day		13th Day		18th Day		25th Day	
		Treat	Check	Treat	Check	Treat	Check	Treat	Check	Treat	Check	Treat	Check	Treat	Check	Treat	Check
1	0	36	25	6	5	7	1	33	39	29	38	24	20	56	57	17	122
2	60	43	13	39	3	51	2	65	27	30	35	21	22	15	78	23	90
3	0	40	12	13	8	20	6	41	38	67	29	28	31	34	45	47	79
4	79	49	19	32	5	67	5	68	43	33	15	16	36	2	83	26	50
5	0	37	16	14	5	12	2	56	30	21	11	27	26	54	90	12	54
6	54	61	18	20	4	80	8	71	47	30	45	18	41	9	83	32	54
7	0	43	15	19	5	48	6	40	34	29	37	24	33	47	118	17	54
8	60	71	14	29	2	75	5	66	37	13	21	10	45	11	100	32	40
9	0	45	11	19	5	30	3	46	45	32	14	18	27	46	69	41	39
10	79	61	17	34	5	76	9	35	23	28	25	8	24	11	76	23	60
11	0	42	7	11	4	29	3	50	21	30	15	22	27	58	116	50	70
12	54	60	9	14	3	89	7	65	24	38	23	19	66	18	106	16	53
13	0	34	10	13	3	41	7	33	21	42	15	42	28	60	123	16	39
14	100	102	10	17	2	87	8	81	21	90	21	9	62	0	100	45	60
15	60	61	14	14	3	78	11	51	20	25	9	21	35	17	145	18	43
16	0	42	10	6	3	33	9	24	19	32	21	47	42	59	95	15	63
17	79	52	5	17	4	71	6	51	20	46	40	24	24	27	137	29	50
18	0	38	6	6	1	29	9	21	18	47	29	22	43	60	86	23	63
19	54	51	14	25	5	72	9	45	25	55	15	21	32	19	92	5	40
20	0	57	9	24	3	26	5	40	20	37	26	35	45	40	100	32	40
21	102	77	9	42	5	105	17	25	16	19	42	5	21	7	104	1	42
22	102	116	11	33	1	75	12	29	18	45	26	14	42	20	114	12	58
23	102	93	12	18	3	75	17	20	32	56	21	24	46	20	100	14	53
24	0	36	7	21	7	75	14	50	18	51	37	22	23	31	122	9	52
25	0	48	8	48	8	70	20	20	30	22	20	25	43	40	77	70	56

Note: "Treat" means a treated plot, while "Check" means an untreated control plot.

Periodic harvesting of all leaves ready and fit for oven curing was made from all plots, and recordings were made of the number of leaves harvested. Harvest data are presented in Table III

Table IV, which follows, shows the difference in harvesting pattern of treated and untreated plants over a period of about two months, the data being discussed further below.

(27)

TABLE IV

Day of Picking	Position of Leaves in Stem In picking Order	Kilos of treated Leaves Suitable for Flue-Curing	(Control) Kilos of Untreated Leaves Suitable for Flue-Curing	Kilos of treated* Leaves not Suitable for Flue-Curing	Kilos of Untreated leaves not Suitable for Flue-Curing
1	1	285		63	13
3	1		160		
5	2	484		24	
9	2	606	690	11	
13	2	554			9
16	2	205	275		
23	3	876		46	
26	3	388		11	48
29	3		195	9	
31	4	795		12	
26	4	176			
29	4			11	
31	4	105		40	
32	5	120		11	
26	5	96			
29	5		345		113
37	3		315		117
41	3		455		11
57	3		235		86
46	4		280		31
57	4		183		39
57	4		95		
59	5				

* Application of the chemical composition of the invention was on day 16, as shown by the horizontal line.

5 Stem: Position of the leaves on the plant stem, position indicating the lowermost leaves with which picking starts, harvesting ending leaves in position 5, the highest two leaves. Kilos. Treated and Control (untreated): Kilos of green-yellow tobacco leaves adequately ripe for picking for oven-curing. Field Control: Kilos of tobacco not suitable for oven-curing and separated for field curing from treated and control plots. The total weight of flue-cured tobacco from treated and untreated plants respectively was 740 kg and 511. The totals of leaves harvested from the treated plants and the control plants were 4690 and 3228, respectively. The average oven curing times for treated and control were 119 hours and 141 hours, respectively. The totals of flue-cured tobacco (kilograms)

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per hectare) were 1390 and 892 for treated and control respectively. The total dry weight of tobacco which, because of unsuitability for flue-curing was left to be field-cured, was 448 kg/ha and 814 kg/ha for treated and control, respectively. (The weight of field cured tobacco is adjusted to calculated total yield per hectare to compensate for 10% more humidity than oven cured.)

It is evident from these data that the application of the composition of the invention

caused a remarkable acceleration of the ripening of the tobacco. Furthermore, a much greater proportion of tobacco leaves became suitable for oven-curing rather than having to be left for field-curing. The curing process was also considerably shortened by about 20 hrs. (from an average of 141 to 119 hours), approximately 15% shortening of curing time; this, even though a greater quantity of tobacco was being cured at one time. Additional data appear in Table V.

TABLE V

Experiment II Results Summary

Treated With Ethephon (100 mg/plant)

Plot Number	I	II	III	IV	Average	V*
Yield/Hectare						
Oven Cured	1100 Kg	1390 Kg	1430 Kg	1085 Kg	1251 Kg	892 Kg
Yield Cured (XO.9)	488	403	400	444	434	733
Total	1588	1793	1830	1529	1685	1625
Percentage						
Oven Cured	69%	78%	78%	71%	74%	55%
Curing Time in						
Oven (Hours)	126	119	119	127	123	141
Ratio of Green						
to Oven Dry	6.3:1					6.3:1

* Control (not treated with ethephon)

From the above, it is to be observed that the increase of oven-cured tobacco is about 30% increase for all treated plots over the control. There was a significant decrease of field-cured tobacco, nearly 50% decrease over the control. There was a greater total of tobacco yield within a certain limited time.

There is a very significant saving in costs of

harvesting and oven-curing when tobacco is treated, in accordance with the invention, compared to the control. Typical of the economic advantages which the product and process of the invention brings about to the tobacco grower and processor is the following as is shown in the Table VI below, where all values are on a per hectare basis.

TABLE VI

Comparison of Costs of Harvesting Treated vs. Untreated Tobacco

	Treated	Untreated	Economic Advantage
Yield Flue-Cured (Kg.)	1,251	892	
Equivalent Green Tobacco×6.3	7,900	5,630	
Flue-Cured Crop Value×\$1.90 (In Dollars)	\$ 15,000	\$ 10,700	\$ 4,300 saved
Average Cost of Harvest (In Dollars) unit/cost	\$ 1,700	\$ 2,900	\$ 1,200 saved

(29)

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From the test plot data obtained in Experiment II, it is possible to derive additional information concerning the dosages suitable for treatment to bring about ripening and harvesting within a preselected time span.

- 5 In particular, for 155 square meter plots of 30 plants (19,300 plants/ha), it can be shown that the number of harvested leaves which has been accumulated as of any given day after

CEPA treatment can be expressed by the formula

$$Y = a + bX + cX^2 \quad (1)$$

where $\bar{Y}$ is the total number of leaves so accumulated and X is the milligrams of ethephon applied per plant.

Using this formula to calculate the yield for application rates of 20, 50 and 100 mg/plant, the Table A below is obtained.

TABLE A

Days from Application to harvest	20 mg/pl	50 mg/pl	100 mg/pl
3	38.6	55.6	84.8
4	54.9	90.2	152.6
6	102.7	229.0	495.4
9	156.7	352.5	788.5
14	190.7	383.6	808.7
17	216.5	389.8	774.3

- 20 Table B, below compares the quantities of harvested leaves with those calculated by means of equation (1) above, for the test plots of Table III. The comparison is made for the quantities accumulated four days after ethephon application. A high degree of consistency is apparent. 25

TABLE B

Consistency of Actual vs. Calculated Values

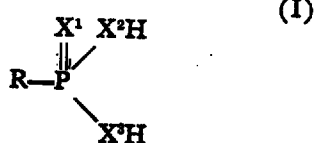
Plot Number	Dosage mg/plant	Harvested Leaves Accumulated 4 Days After Application	
		Actual	Calculated
1	9	42	42
2	42	82	77
3	21	53	55
4	55	81	91
5	20	51	54
6	38	81	73
7	17	62	51
8	42	100	77
9	21	64	55
10	55	95	91
11	20	53	54
12	38	74	73
13	23	47	57
14	79	119	105
15	57	75	93
16	21	48	55
17	55	69	91
18	20	44	54
19	38	76	73
20	23	81	57
21	87	119	122
22	102	149	136
23	87	111	122
24	15	57	49
25	0	16	

It is apparent that in accordance with the invention, it is possible to determine one or more of the variables in equation (1) from the knowledge of the other variables. It is, thus possible to determine the total number of leaves which will ripen upon application of a given weight of the composition of the invention and hence allow for timing and controlled production and harvesting of the tobacco; conversely if the weight and timing of the desired harvest is preselected, a minimum amount of the composition of the invention shall be determinable.

A major improvement made possible by the invention is the enhancement of the chemical and physical properties of the tobacco leaves. The acceleration of leaf ripening which the invention brings about causes a number of the undesirable chemical components of the plant either to stay in the stalk or to recede to the stalk if they have begun to enter the leaves. The desirable chemical elements, such as sugars, are encouraged to move into or stay in the leaves at the time they are picked. The accelerated curing which the invention makes possible serves to provide an end product which has the resiliency desired for tobacco leaf wrapper for cigars, and yet may be cut for cigarettes or pipe tobacco purposes without undesirable powdering of the tobacco.

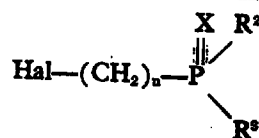
WHAT WE CLAIM IS:—

1. A process for accelerating the ripening of tobacco leaves, preparatory to their harvesting and curing, in which to the leaf, when it is fully-developed and has reached physiological maturity, there is applied while the leaf is still fresh an effective amount, not exceeding 200 milligrams per tobacco plant, of one or more phosphonic acid compounds which conform to the general formula



(where X^1 , X^2 and X^3 , which may be the same or different, are each oxygen or sulphur; and R is an alkyl or alkenyl group, optionally substituted by one or more hydroxy, alkoxy, amino, substituted amino or quaternized amino, halo, cyano, carboxyl, sulphonamido or phosphono groups) or corresponding functional derivatives thereof being salts, hydrolyzable esters, amides, acid halides or anhydrides formed with the $-\text{X}^2\text{H}$ and/or $-\text{X}^3\text{H}$ groups of the phosphonic acid compounds of general formula I above.

2. A process as claimed in claim 1, in which the phosphonic acid compounds of general formula I used in the process conform to the



wherein:

- X represents oxygen or sulphur;
- n is an integer from 1 to 6;
- Hal represents a halogen atom; and
- R^2 and R^3 both represent either hydroxy groups or amino groups, or one of them represents a hydroxy group while the other represents an alkoxy or substituted-alkoxy group, or R^2 and R^3 together represent the residue of an anhydride.

3. A process as claimed in claim 2, in which the phosphonic acid compound(s) and/or functional derivatives thereof used in the process is/are 2-halo-ethyl phosphonic acids and the salts, hydrolyzable esters and amides thereof.

4. A process as claimed in claim 3, in which the phosphonic acid compound used is 2-chloroethyl phosphonic acid.

5. A process as claimed in any of claims 1 to 4, in which the phosphonic acid compound(s) and/or functional derivative(s) thereof is/are applied to the plant only after substantially all the leaves are fully-developed and have reached physiological maturity and while the leaves are still fresh.

6. A process as claimed in claim 5, in which the already fully-developed lower leaves are gathered, prior to the application, by the priming system.

7. A process as claimed in claim 6, in which the application takes place after the second priming.

8. A process as claimed in any of claims 1 to 7, in which the amount of phosphonic acid compound(s) and/or derivative(s) thereof applied per plant is in the range of from 50 to 150 milligrams.

9. A process as claimed in any of claims 1 to 8, in which the phosphonic acid compound(s) and/or functional derivatives thereof are applied in the form of compositions wherein they are mixed with suitable carriers for agricultural compositions.

10. A process as claimed in claim 9, in which the amount of phosphonic acid compound(s) and/or functional derivative(s) applied to the crop of tobacco plants is at a rate of about 2 pounds per acre dissolved in about 40—50 United States gallons of water.

11. A process as claimed in claim 9, in which the composition applied to the tobacco plant contains between 0.04 and 0.4 pounds of the phosphonic acid compound(s) and/or derivatives per U.S. gallon of liquid carrier.

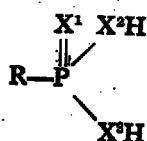
12. A process as claimed in claim 11, in which the composition applied to the tobacco plant is made up by diluting a concentrate with water, said concentrate containing from

It is apparent that in accordance with the invention, it is possible to determine one or more of the variables in equation (1) from the knowledge of the other variables. It is, thus possible to determine the total number of leaves which will ripen upon application of a given weight of the composition of the invention and hence allow for timing and controlled production and harvesting of the tobacco; conversely if the weight and timing of the desired harvest is preselected, a minimum amount of the composition of the invention shall be determinable.

A major improvement made possible by the invention is the enhancement of the chemical and physical properties of the tobacco leaves. The acceleration of leaf ripening which the invention brings about causes a number of the undesirable chemical components of the plant either to stay in the stalk or to recede to the stalk if they have begun to enter the leaves. The desirable chemical elements, such as sugars, are encouraged to move into or stay in the leaves at the time they are picked. The accelerated curing which the invention makes possible serves to provide an end product which has the resiliency desired for tobacco leaf wrapper for cigars, and yet may be cut for cigarettes or pipe tobacco purposes without undesirable powdering of the tobacco.

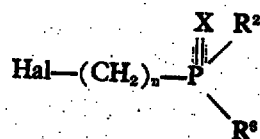
WHAT WE CLAIM IS:—

1. A process for accelerating the ripening of tobacco leaves, preparatory to their harvesting and curing, in which to the leaf, when it is fully-developed and has reached physiological maturity, there is applied while the leaf is still fresh an effective amount, not exceeding 200 milligrams per tobacco plant, of one or more phosphonic acid compounds which conform to the general formula



(where X^1 , X^2 and X^3 , which may be the same or different, are each oxygen or sulphur; and R is an alkyl or alkenyl group, optionally substituted by one or more hydroxy, alkoxy, amino, substituted amino or quaternized amino, halo, cyano, carboxyl, sulphonamido or phosphono groups) or corresponding functional derivatives thereof being salts, hydrolyzable esters, amides, acid halides or anhydrides formed with the $-\text{X}^1\text{H}$ and/or $-\text{X}^3\text{H}$ groups of the phosphonic acid compounds of general formula I above.

2. A process as claimed in claim 1, in which the phosphonic acid compounds of general formula I used in the process conform to the



wherein:

X represents oxygen or sulphur;

n is an integer from 1 to 6;

Hal represents a halogen atom; and

R^2 and R^3 both represent either hydroxy groups or amino groups, or one of them represents a hydroxy group while the other represents an alkoxy or substituted-alkoxy group, or R^2 and R^3 together represent the residue of an anhydride.

3. A process as claimed in claim 2, in which the phosphonic acid compound(s) and/or functional derivatives thereof used in the process is/are 2-halo-ethyl phosphonic acids and the salts, hydrolyzable esters and amides thereof.

4. A process as claimed in claim 3, in which the phosphonic acid compound used is 2-chloroethyl phosphonic acid.

5. A process as claimed in any of claims 1 to 4, in which the phosphonic acid compound(s) and/or functional derivative(s) thereof is/are applied to the plant only after substantially all the leaves are fully-developed and have reached physiological maturity and while the leaves are still fresh.

6. A process as claimed in claim 5, in which the already fully-developed lower leaves are gathered, prior to the application, by the priming system.

7. A process as claimed in claim 6, in which the application takes place after the second priming.

8. A process as claimed in any of claims 1 to 7, in which the amount of phosphonic acid compound(s) and/or derivative(s) thereof applied per plant is in the range of from 50 to 150 milligrams.

9. A process as claimed in any of claims 1 to 8, in which the phosphonic acid compound(s) and/or functional derivatives thereof are applied in the form of compositions wherein they are mixed with suitable carriers for agricultural compositions.

10. A process as claimed in claim 9, in which the amount of phosphonic acid compound(s) and/or functional derivative(s) applied to the crop of tobacco plants is at a rate of about 2 pounds per acre dissolved in about 40—50 United States gallons of water.

11. A process as claimed in claim 9, in which the composition applied to the tobacco plant contains between 0.04 and 0.4 pounds of the phosphonic acid compound(s) and/or derivatives per U.S. gallon of liquid carrier.

12. A process as claimed in claim 11, in which the composition applied to the tobacco plant is made up by diluting a concentrate with water, said concentrate containing from

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- 30% to 95% by weight of the phosphonic acid compound(s) and/or functional derivative(s) thereof.
- 5 13. A process as claimed in claim 12, in which the concentrate contains 40%—60% by weight of said compound(s) and/or derivative(s).
- 10 14. A process as claimed in any of claims 9 to 13, in which the composition comprises an aqueous solution containing one or more stabilizers.
- 15 15. A process as claimed in claim 14, in which the stabilizer is or includes one or more acids and/or buffers, such that the pH of the concentrate is not greater than 5.
- 20 16. A process as claimed in claim 14 or claim 15, in which the stabilizer is or includes polyethylene glycol.
17. A process of harvesting and curing a tobacco crop, as claimed in any of claims 1 to 16, in which the curing-period for tobacco to which has been applied an effective amount of one or more of the phosphonic acid compound(s) of general formula I and/or the aforesaid functional derivative(s) thereof is determined, and successive applications thereof are made at time-intervals substantially the same as that curing-period, each successive application being made only to a section of the crop corresponding in size to the curing-capacity available, so that each crop-section becomes ripe and ready for harvesting and curing as the previously harvested crop-section completes its curing.
- 25 18. Processes for accelerating the ripening of tobacco, and for harvesting and curing a tobacco crop, as claimed in any of the preceding claims and substantially as herein described.
- 35 19. Tobacco, whenever ripened, harvested and cured by the process claimed in any of the preceding claims.
- 40

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