

PATENT SPECIFICATION

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(54) PLANT GROWTH REGULANT

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, 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 plant growth regulants, particularly compositions which release ethylene in a controlled manner.

UK Patent Specification No. 1315131 describes and claims a composition comprising a volatile or gaseous plant growth regulant and a solid non-volatile adsorbent material dispersed in a viscous fluid medium, at least a part of the volatile or gaseous plant growth regulant being releaseably adsorbed on the surface of the non-volatile adsorbent material. The plant growth regulant may be ethylene, the solid non-volatile adsorbent material may be an aluminosilicate, known as a zeolite or molecular sieve, and the viscous fluid medium may be a mineral oil.

The plant growth regulant is particularly useful in stimulating the production of rubber latex from rubber trees such as *Hevea brasiliensis*, being applied to the trees close to the tapping cut. A satisfactory plant growth regulant should therefore have the capacity to hold the ethylene during storage, to release it at a controlled rate when applied to the tree, and to exhibit these characteristics under the conditions of high temperature and humidity normally found in rubber-producing areas of the world.

In their investigations into the most suitable non-volatile adsorbent material satisfying the above conditions the applicants have confirmed that zeolites are suitable adsorbents for the ethylene but that not all zeolites are equally effective. In particular they have found that the capacity of a zeolite to adsorb, hold, and desorb ethylene depends on its water content and that some zeolites are much less critical than others in their relationship between water content and ethylene adsorption. Since as indicated above, the plant growth regulants are likely to be stored, used, and, possibly, manufactured in humid climates, it follows that a zeolite whose ethylene adsorption is less affected by water content is to be preferred.

According to the present invention a composition comprising a gaseous plant growth regulant, which is ethylene, acetylene or propylene, and a solid non-volatile adsorbent material dispersed in a viscous fluid medium is characterised in that the adsorbent material is a relatively anhydrous zeolite, as hereinafter defined the metal cation of the zeolite being a Group II metal cation.

The preferred plant growth regulant is ethylene.

The preferred zeolite is the 5Å pore size Zeolite A preferably having a calcium or magnesium cation. As is well known the sodium form of Zeolite A has a pore size of 4Å. The pore size increases to 5Å if the monovalent sodium cation is replaced by a divalent cation, e.g. calcium or magnesium. Ethylene is adsorbed by both the 4Å and 5Å versions of Zeolite A, the maximum theoretical capacity being the same if the zeolite is completely anhydrous. As will be discussed in more detail hereafter, however the actual capacity depends very much on the amount of water present.

Zeolite A is produced commercially in both binderless and binder-containing versions. The former is preferred since the overall ethylene capacity is greater, but it has been found that the presence of a binder e.g. clay, alumina or sepiolite has no other major adverse effect. Previously used zeolites e.g. spent zeolites from a molecular sieve n-paraffin separation process may have a lower capacity than fresh zeolites but, again, have no other disadvantages

apart from this, and may be a cheap source of zeolites. The zeolite may be in the form of particles having a particle size of from 1 to 20 microns.

The zeolite should, as indicated above, be relatively anhydrous to allow for a significant uptake of ethylene but, as previously explained, the zeolites used in the present invention show less criticality than other zeolites in their relationship between water content and ethylene uptake. In practice it is not necessary to have very low water contents and the term "relatively anhydrous zeolite" as used in this specification means a zeolite with up to 10% wt of water, preferably up to 5% wt. of water. Thus, commercially available pre-calcined zeolites may be used without the need for any further calcination or dehydration steps.

The viscous fluid medium serves to seal the plant growth regulant in the zeolite, to control its release, and to facilitate the application of the composition to plants. It should obviously not be toxic to plants. The term viscous fluid medium does not imply that it is necessarily liquid at atmospheric temperatures, and the viscosity may be chosen, by means of simple experiments if necessary, so that the fluid medium effectively achieves the three objectives indicated above. It preferably has a melting point of 50 to 90°C so that it is solid at atmospheric temperatures but can be rendered fluid at moderately elevated temperatures to facilitate the incorporation of the zeolite during manufacture. It preferably also has a yield stress greater than 10 and less than 1000 newtons/metre² at 35°C, and a stress of less than 1,000 newtons/metre² at a shear rate of 10 reciprocal seconds at 35°C. Suitable media may be animal, vegetable or mineral fats, oils, jellies or waxes. For ready availability and cheapness, fractions derived from petroleum are preferred, particularly fractions boiling in the range 370 to 550°C. A preferred petroleum fraction is a distillate lubricating oil fraction to which has been added sufficient wax, e.g. slack wax, to give the required melting point and viscosity characteristics. Suitably from 30 to 70% wt. of slack wax, by weight of oil, may be added to lubricating oil having a viscosity of from 50 to 200 centistokes at 100°F (37.8°C).

The maximum plant growth regulant capacity of the zeolite may be determined by standard adsorption tests and will be about 7g/100g of zeolite for ethylene and an anhydrous zeolite. The weight of zeolite containing the plant growth regulant is also chosen, in relation to the weight of viscous fluid medium so that the three objectives indicated above for the viscous fluid medium are achieved. Again, simple experiments may be used, if necessary. The weight may conveniently be from 10 to 25g/100g of total composition. In practice convenient levels of ethylene in the zeolite and zeolite in the total composition are such as to give ethylene contents of 5 to 12 ml of ethylene/g of total composition.

The preparation of the composition involves only the two simple stages of adsorbing the ethylene into the zeolite and then mixing the zeolite into the viscous fluid medium. The ethylene may be adsorbed by subjecting the zeolite to an atmosphere of ethylene in a closed vessel at a temperature of 0 to 50°C and a pressure of 0 to 5 atmospheres gauge. Air may be removed from the vessel and the zeolite by a preliminary purging with nitrogen and the application of a vacuum of less than 100 torr (4 inches Hg). Uptake of ethylene into an evacuated zeolite is rapid particularly at elevated pressure and the uptake time may be from 2 to 10 minutes. The zeolite containing adsorbed ethylene is then mixed with the viscous fluid medium by stirring it in to the medium, which is heated as necessary to render the medium liquid. A convenient temperature may be from 50 to 100°C and the stirrers used and speed of rotation should be selected to minimise incorporation of gas into the mixture. The mixture may be fed into containers for storage and transport at the mixing temperature or slightly below.

The preparation may use a single vessel or, preferably, two interconnected vessels. In a single vessel the zeolite may be placed on the surface of the medium at a temperature at which the medium is solid and the ethylene admitted to the free space above the zeolite layer. The medium is then heated to melt it and the zeolite stirred in, the ethylene atmosphere being maintained if desired. With two interconnected vessels, one holds the zeolite and the ethylene and the other holds and heats the viscous fluid medium. Either vessel may be used for bringing the zeolite and medium together and mixing, but preferably the zeolite containing adsorbed ethylene is transferred to the vessel with the heated viscous fluid medium.

The method of application of the composition to the plant and the amount used will depend on the plant and the purpose of the application. As previously indicated, a preferred use is to stimulate the yield of rubber latex from rubber trees, particularly *Hevea brasiliensis* and details of amounts used and methods of application may be as described in UK patent specification No. 1315131.

The invention is illustrated by the following examples.

Example 1

In this example fundamental data on ethylene adsorption and its relation to water content were obtained. The following zeolites were used

1. Zeolite 4A - as a 1-5 microns powder.

2. Zeolite 5A - a binderless zeolite supplied as 3mm tablets and subsequently ground to a

particle size of less than 160 microns.

3. Zeolite 5 - a zeolite with binder supplied as 3mm balls and ground as for 2 above.

4. Spent Zeolite 5A - as for 3 above but discharged from a n-paraffin separation plant after 6 years of use.

These 4 zeolites were tested for ethylene capacity at various water contents using ethylene of >99% purity supplied by the British Oxygen Company.

The results obtained are shown in the graphs the provisional specification in which

Figure 1 shows the ethylene adsorbed against time using relatively anhydrous sieves

Figure 2 shows the ethylene adsorbed against the water content of the zeolite

Figure 3 shows the ethylene adsorbed after exposure of the zeolite to air at ambient temperature and humidity, and

Figure 4 shows the water adsorbed against time.

The ethylene capacities shown in Figure 1 were determined in the following manner:-

25g of the zeolite under test were dried in a flask under nitrogen for 2½ hours at 250°C and then cooled back in a flow of nitrogen. The flask was quickly stoppered, transferred to a 1/2 litre autoclave to prevent any ingress of moisture and broken by a thermo-couple pocket as the flask was being bolted down. Ethylene was admitted rapidly until the final pressure in the autoclave was 3 bar(ga) at ambient temperature. The pressure drop observed in the autoclave was converted to a weight of ethylene and the results expressed as grams of ethylene adsorbed per 100 grams of zeolite.

The ethylene capacities shown in Figures 2 and 3 were determined by exposing the zeolites for appropriate times to air at ambient conditions in the glass liner of the autoclave. The glass liner was then sealed with Parafilm sealing tissue whilst being transferred to the autoclave. The sealing tissue was removed as the autoclave was bolted down. The ethylene capacity was then determined as for Figure 1.

The water capacities of Figure 4 were determined by calcining the zeolites in an oven at 550°C for 3 hours and then cooling in a desiccator. The zeolites were then exposed to the air at ambient temperature and humidity and samples taken at set intervals. The samples were weighed, calcined and cooled as above and reweighed, the weight loss being taken as the water content.

Figure 1 shows that the fresh zeolites 1 to 3 were not completely anhydrous even after heating to 250°C in nitrogen for 2 1/2 hours. At water levels of about 1% wt. the 4A zeolite (1) initially adsorbed ethylene more quickly but the total ethylene uptake for the 5A zeolites (2 and 3) was higher, with the binderless zeolite (2) having the highest capacity. The used 5A zeolite (4) was only marginally inferior to the fresh 4A zeolite (1). The used 5A zeolite did, however, have a very low water content.

The inter-relationship between ethylene uptake and water content is illustrated in Figure 2. It will be seen that the ethylene capacity of the 4A zeolite (1) drops very quickly with increase in water content. The drop for 5A zeolite (2, 3, 4) is more gradual so that they have a higher ethylene capacity at all water levels above 1%. The capacities of the 5A zeolites are in the order fresh-binderless (2), fresh-bound (3) and used bound (4), although the effect of the binder is less marked at high water contents.

Figure 3 shows that the binderless 5A zeolite (1) has the greatest ethylene uptake after exposure to air at ambient conditions for all exposure times less than 3 hours. The 4A zeolite has the lowest ethylene uptake after all exposure times (4).

Figure 4 shows that the three fresh zeolites (1,2,3) take up water at approximately the same rate but that the spent zeolite (4) has only a slow uptake of water.

The significance of the results shown in Figures 1 to 4 for the practical use of plant growth regulants is as follows:-

Figure 1 shows that the time for maximum ethylene adsorption is similar for all 4 zeolites and is relatively rapid. Increasing the adsorption time beyond about 10 minutes gives only a small further increase in ethylene adsorption.

Figure 2 shows that the adsorption of ethylene is very dependent on water content and that the water content has a less marked effect on the ethylene uptake 5A than of 4A zeolites. As previously explained, this gives 5A zeolites obvious advantages in manufacture, storage and use, particularly in warm, humid climates.

Figure 3 gives an indication of the handling advantages of the 5A zeolites in that 5A zeolites can be exposed to air for considerably longer periods than 4A sieves whilst still giving an acceptable uptake of ethylene.

Figure 4 shows that the differences observed in Figures 2 and 3 are not due to the difference in rate of water uptake since the rate of water uptake is the same for fresh 4A and 5A. The difference in behaviour is believed to be due to the different locations of the cations in 4A and 5A zeolites. Interaction of the water molecules with the cations in the 4A zeolites restricts ethylene adsorption.

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Example 2

Preparation of a plant growth regulant in a single container.

A series of runs was carried out. The general procedure used was as follows:

(a) A suitable quantity (3 l) of an oil/slack wax mixture was charged to a 1 gallon vessel

(b) when the mixture was level the required quantity of precalcined zeolite was added and the lid of the vessel quickly bolted down

(c) the vessel was purged with nitrogen and then evacuated

(d) ethylene gas was introduced under positive pressure

(e) when the absorption of ethylene has ceased the mixture was heated to about 70°C and stirred to disperse the zeolite. An ethylene atmosphere was maintained and twin marine propellor stirrers were used

(f) the mixture was cooled to 40°C and drained from the vessel

(g) the ethylene content of each run was measured in duplicate.

The oil for the mixture was a lubricating oil having a viscosity of 110 cs. at 100°F. The slack wax was a micro-crystalline wax having a congealing point of 150°F (65°C), an oil content of 12% wt., (ASTM D721) and a specific gravity at 60°F/60°F of 0.89.

A first series of runs compared the ethylene contents of compositions using a 4A zeolite ex Laporte Industries Limited, and a 5A zeolite ex Union Carbide Ltd. Both zeolites were first calcined overnight at 475°C and cooled under vacuum.

Both the 4A and 5A zeolite compositions used the same proportions viz:

Zeolite 22.5% wt.

Oil 52.0% wt.

Slack wax 25.5% wt.

The results are shown in Table 1 below.

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Table 1

Zeolite used	Ethylene adsorption		Temp (°C)	Mixing		Ethylene content mls/g
	No. of N ₂ purges at 45 psi	Vacuum time (mins.)		Ethylene adsorption at 45 psi (mins)	Stirrer speed (rpm)	
4A	3	2	80	700	60	2.6
	3	15	62	700	60	1.2) 1.5)
	0	60	71	700	60	3.0) 3.1)
	3	45	70	700	60	11.5) 11.9)
5A	3	60	75	700	60	9.7) 10.9)
	3	45	75	700	90	9.7) 11.0)

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Table 1 clearly shows the much greater effectiveness of the 5A zeolite.

A second series of runs used zeolites pre-calcined by the manufacturers and used directly without any further calcination. The zeolites were a 4A zeolite ex W.R. Grace & Co. Ltd containing 4.1% wt. of water and a 5A zeolite ex Laporte Industries Limited, containing 7.45% wt. water. The results are shown in Table 2.

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Table 2

Zeolite type	% Composition		Vacuum Time (mins)	C ₂ H ₄ Absorption Time at 45 psi (mins)	Temp °C	Stirrer Speed (rpm)	Stirring time (mins)	C ₂ H ₄ content (ml/g)
	Zeolite	Oil						
Grace 4A	22.5	62.5	30	3	70	500	50	10.5) 10.6)
Laporte 5A	22.5	62.5	20	3	70	500	30	12.1) 12.1)
Laporte 5A	12.5	62	20	3	70	500	60	7.3) 7.1)

Table 2 confirms the superiority of the 5A zeolite which had a higher ethylene uptake than the 4A zeolite despite a considerably higher water content. The table also shows that ethylene adsorption times of only 3 minutes at 45 psi are adequate and that, at a zeolite content of only 12.5% wt., an ethylene content of 7 ml/g of total composition is achievable.

5 Example 3

Preparation of a plant growth regulant in a twin vessel system.

Two 1 gallon vessels were linked by a jacketed transfer tube. An oil/slack wax mixture was heated to 75°C in one vessel and Laporte 5A zeolite placed in the other, the proportions being the same as the second run of Table 2. The zeolite vessel was purged with nitrogen and evacuated 3 times and ethylene introduced at an initial pressure of 45 psi. After 3 mins absorption was complete.

The zeolite was heated to 70° and the hot oil/wax moisture transferred from the other vessel using 40 psi nitrogen. The mixture was stirred at 500 rpm using twin brumigin stirrers for 30 mins. A good homogeneous product having an ethylene content of 12 ml/g was obtained with very little aeration.

15 Example 4

Rate of ethylene release.

To study the rate of ethylene release from compositions prepared as in the previous examples, wet nitrogen at 50 ml/min was passed continuously over samples containing various 5A zeolites at various zeolite contents. The experiment was carried out at 30° and 72% humidity with 4 g of each sample spread 87 mm x 13 mm about 3 mm thick onto foil. This simulated conditions for a rubber tree in Malaysia.

Ethylene contents were measured in duplicate over 13 weeks, about the expected useful life of the composition on the tree.

After an initial relatively high rate of ethylene loss, ethylene release remained relatively steady for the 13 weeks. The compositions used and the average weekly rate of ethylene loss are shown in Table 3 below.

Table 3

Zeolite used	Composition			Initial Ethylene content ml/g	Average rate of ethylene release ml/g/week
	Zeolite	Oil	Wax		
Union Carbide 5A	22.5	52	25.5	10.4	0.12
Laporte 5A	11	59	30	6.4	0.25
W.R. Grace 5A	12.5	62	25.5	4.1	0.16

The initial water contents of the zeolites were:- Union Carbide % wt. Laporte 7.45% wt. and W.R. Grace 14.7% wt. The relatively high water content of the latter zeolite explains the relatively low initial ethylene content, but the results show that the rate of release of ethylene is independent of the initial ethylene content.

30 WHAT WE CLAIM IS:-

1. A composition comprising a gaseous plant growth regulant which is ethylene, acetylene or propylene, and a solid non-volatile adsorbent material dispersed in a viscous fluid medium, characterised in that the adsorbent material is a relatively anhydrous zeolite as hereinbefore defined the metal cation of the zeolite being a Group II metal cation.

2. A composition as claimed in claim 1 wherein the zeolite is a 5Å pore size Zeolite A.

3. A composition as claimed in claim 1 or 2 wherein the Group II metal cation is calcium or magnesium.

4. A composition as claimed in any claim 1 to 3 wherein the viscous fluid medium has a melting point of 50 to 90°C.

5. A composition as claimed in any of claims 1 to 4 wherein the viscous fluid medium has a yield stress greater than 10 and less than 1000 newtons/metre² at 35°C and a stress of less than 1000 newtons/metre² at a shear rate of 10 reciprocal seconds at 35°C.

6. A composition as claimed in any of claims 1 to 5 wherein the viscous fluid medium is a petroleum fraction boiling in the range 370 to 550°C.

7. A composition as claimed in claim 6 wherein the petroleum fraction is a lubricating oil having a viscosity of from 50 to 200 centistokes at 100°F admixed with from 30 to 70% wt of

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WHAT WE CLAIM IS:-

1. A composition comprising a gaseous plant growth regulant which is ethylene, acetylene or propylene, and a solid non-volatile adsorbent material dispersed in a viscous fluid medium, characterised in that the adsorbent material is a relatively anhydrous zeolite as hereinbefore defined the metal cation of the zeolite being a Group II metal cation.
2. A composition as claimed in claim 1 wherein the zeolite is a 5A pore size Zeolite A.
3. A composition as claimed in claim 1 or 2 wherein the Group II metal cation is calcium or magnesium.
4. A composition as claimed in any claim 1 to 3 wherein the viscous fluid medium has a melting point of 50 to 90°C.
5. A composition as claimed in any of claims 1 to 4 wherein the viscous fluid medium has a yield stress greater than 10 and less than 1000 newtons/metre² at 35°C and a stress of less than 1000 newtons/metre² at a shear rate of 10 reciprocal seconds at 35°C.
6. A composition as claimed in any of claims 1 to 5 wherein the viscous fluid medium is a petroleum fraction boiling in the range 370 to 550°C.
7. A composition as claimed in claim 6 wherein the petroleum fraction is a lubricating oil having a viscosity of from 50 to 200 centistokes at 100°F admixed with from 30 to 70% wt of



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slack wax by weight of the lubricating oil.

8. A composition as claimed in any of claims 1 to 7 wherein the composition contains from 10 to 25 g of zeolite containing the adsorbed plant growth regulant/100 g of total composition.

9. A composition as claimed in claim 1 wherein the plant growth regulant is ethylene present in an amount of from 5 to 12 ml/g of total composition.

10. A method of preparing a composition as claimed in any of claims 1 to 9 wherein the zeolite is purged with inert gas and/or evacuated to remove air, is subjected to an atmosphere of the plant growth regulant at 0 to 50°C and 0 to 5 atmospheres gauge and is then stirred into the viscous fluid medium.

11. A method of stimulating the production of rubber latex from rubber trees comprising applying to the tree a composition as claimed in any of claims 1 to 9 or a composition prepared as claimed in claim 10.

12. A composition as claimed in any of claims 1 to 9 substantially as described in Examples 2 to 4.

13. A method as claimed in claim 10 substantially as described in Examples 2 and 3.

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