H0853 PCT/AU

SPRUSON & FERGUSON

Australia

Patents Act 1990

NOTICE OF ENTITLEMENT

I, Dr. Georg Zeit. of Falkenweg 2, 40764 Langenfeld/ Federal Republic of Germany, being authorised by the Applicant/Nominated Person in respect of Application No 74925/94 state the following:-

The Applicant/Nominated Person has entitlement from the actual inventor(s) as follows:-

The Applicant/Nominated Person, by virtue of a Contract between the actual inventor(s) as employee(s) and the Applicant/Nominated Person as employer, is a person which would be entitled to have the patent assigned to it if a patent were granted on an application made by the actual inventor(s).

The Applicant/Nominated Person is the applicant of the application(s) listed in the Declaration under Article 8 of the PCT. The basic application(s) listed on the Declaration under Article 8 of the PCT is/are the application(s) first made in a Convention country in respect of the invention.

DATED this NINETEENTH day of JANUARY 19 96

Dr. Georg Zeit

Dr Georg Zeit

IRN: ~~168548x~~ 315651

INSTR CODE: 55370

9826D/GMM

AU9474925

(12) PATENT ABRIDGMENT (11) Document No. AU-B-74925/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 678283

(54) Title
USE OF SELECTED POLYVINYL ACETATE DISPERSIONS FOR SOLIDIFYINGTHE SURFACE OF SAND AND/OR EARTH

International Patent Classification(s)
(51)[6] C09K 017/20 C09K 017/14 E21B 043/02

(21) Application No. : 74925/94 (22) Application Date : 12.07.94

(87) PCT Publication Number : WO95/03372

(30) Priority Data

(31) Number	(32) Date	(33) Country
4324474	21.07.93	DE GERMANY

(43) Publication Date : 20.02.95

(44) Publication Date of Accepted Application : 22.05.97

(71) Applicant(s)
HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN

(72) Inventor(s)
WOLFGANG RITTER; STEPHAN VON TAPAVICZA; HEINZ MULLER; HARTMUT BUSCHING

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
US 4072020
US 3887503
GB 906470

(57) Claim

1. A method of surface stabilization of sand and/or soil, which method comprises applying to the sand and/or soil an aqueous polyvinyl acetate dispersion containing at least one biodegradable plasticizer selected from a triester of glycerol with lower aliphatic monocarboxylic acids, a citric acid triester with lower aliphatic monohydric alcohols and/or an epoxidized triglyceride of at least partly olefinically unsaturated fatty acids.

OPI DATE 20/02/95 APPLN. ID 74925/94
AOJP DATE 30/03/95 PCT NUMBER PCT/EP94/02284
AU9474925

(51) Internationale Patentklassifikation 6 :
C09K 17/20, E21B 43/02, C09K 17/14

A1

(11) Internationale Veröffentlichungsnummer: WO 95/03372

(43) Internationales Veröffentlichungsdatum: 2. Februar 1995 (02.02.95)

(21) Internationales Aktenzeichen: PCT/EP94/02284

(22) Internationales Anmeldedatum: 12. Juli 1994 (12.07.94)

(30) Prioritätsdaten:
P 43 24 474.2 21. Juli 1993 (21.07.93) DE

(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; D-40191 Düsseldorf (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: RITTER, Wolfgang [DE/DE]; Am Bandenfeld 74, D-42781 Haan (DE). VON TAPAVICZA, Stephan [DE/DE]; Thomas-Mann-Strasse 12, D-40699 Erkrath 2 (DE). MÜLLER, Heinz [DE/DE]; Sperberstrasse 5, D-40789 Monheim (DE). BÜSCHING, Hartmut [DE/DE]; Glissen 49, D-31604 Raddestorf (DE).

(81) Bestimmungsstaaten: AU, JP, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht
Mit internationalem Recherchenbericht

678283

(54) Title: USE OF SELECTED POLYVINYL ACETATE DISPERSIONS FOR SOLIDIFYING THE SURFACE OF SAND AND/OR EARTH

(54) Bezeichnung: VERWENDUNG AUSGEWÄHLTER POLYVINYLACETAT-DISPERSIONEN FÜR DIE OBERFLÄCHENVERFESTIGUNG VON SAND UND/ODER ERDREICH

(57) Abstract

The description relates to the use of glycerine triesters with lower aliphatic mono-carboxylic acids, citric acid triesters with lower aliphatic monofunctional alcohols and/or epoxidised triglycerides of at least olefinically unsaturated fatty acids as bio-degradable softeners in aqueous polyvinyl acetate dispersions for use in solidifying the surface of sand and/or earth.

(57) Zusammenfassung

Beschrieben wird die Verwendung von Triestern des Glycerins mit niederen aliphatischen Monocarbonsäuren, Citronensäuretriestern mit niederen aliphatischen monofunktionellen Alkoholen und/oder epoxidierten Triglyceriden wenigstens anteilsweise olefinisch ungesättigter Fettsäuren als biologisch abbaubare Weichmacher in wäßrigen Polyvinylacetat-Dispersionen für deren Einsatz zur Oberflächenverfestigung von Sand und/oder Erdreich.

The use of selected polyvinyl acetate dispersions for the surface stabilization of sand and/or soil

This invention relates to the surface stabilization of sand and/or soil, hereinafter generally referred to as soil, by application and introduction of an aqueous polymer dispersion to and into surface layers of soil. The water in the impregnating composition introduced dries in a comparatively short time and the polymer phase remaining behind solidifies the structure, for example the granular structure, of the impregnated soil without unduly affecting the permeability of these layers to water. Surface stabilization such as this is not confined to soil in the narrower sense. The corresponding stabilization of other surface zones which have to be protected, for example, against wind erosion falls within the scope of the teaching according to the invention. Examples of such surface zones include spoil banks with or without application of a covering of top soil or the like.

Development and practice have been concerned for decades with the concept - on which the present invention is also based - of applying synthetic polymers which cause particulate solids to adhere to one another to the surfaces to be stabilized in the form of aqueous dispersions or emulsions and leaving them to dry thereon. Aqueous polyvinyl acetate dispersions, hereinafter also referred to as PVAc dispersions, are of particular significance in this regard, cf. A. Kullmann et al. in **Archiv für Acker- und Pflanzenbau und Bodenkunde, Vol. 22, No. 11 (1978), pages 713 to 719 (Chemical Asbtracts 91 (5): 38081u).** Besides polyvinyl acetate, butadiene/styrene latex, a urea/formaldehyde polymer and a bitumen emulsion are described as useful binders. The corre-

AUSTRALIAN PATENT OFFICE

sponding stabilization of dune sand against the effects of rain is the subject of an article by D. Gabriels et al. **in Soil Science, Vol. 118, No. 5 (1974), pages 332 to 338 (Chemical Abstracts 82 (15): 96945d).** In this publication, too, a binder system based on polyvinyl acetate is included among the preferred binders. **US-A-4,072,020, US-A-3,887,506, Chemical Abstracts 85 (21): 158730c (= HU-A-11 654)** and **ZA-A-7501787** are mentioned as examples of the other works being carried out worldwide.

The list of requirements or functions to be fulfilled by corresponding stabilization of the earth's surface can be extremely diverse. Without any claim to completeness, some of the properties required in practice are mentioned in the following: the material should be resistant at least to pedestrian traffic, it should not be affected by the particular temperatures prevailing, atmospheric humidity or rain (for the period envisaged) and should also be resistant to high wind speeds. The material to be applied should be non-inflammable and should not represent a fire or explosion risk either in storage or during and after its application. Its transport and application should not entail any exceptional protective measures or the wearing of protective clothing. The cured polymer impregnation should not have any toxic effect on germinating plants, on growing plants or on animals and should be colorless or transparent. Taking these and other requirements into account, the present state of the art may be summarized as follows:

1. PVAc homopolymer dispersions are basically suitable as binders. In the absence of plasticizers, however, the cohesion of the soil layers impregnated with PVAc homopolymer dispersions is so brittle that key application requirements are not satisfied.

AUSTRALIAN PATENT OFFICE 13

2. The deficiency mentioned in (1) can be eliminated by using plasticizers capable of flow under normal conditions. In practice, dibutyl phthalate has proved to be a particularly effective plasticizer. Correspondingly plasticized PVAc homopolymers provide for firm cohesion although the plasticizer is non-degradable.

3. Internally plasticized polymer dispersions (polyvinyl acetate co-dibutyl maleate) provide for firm cohesion but are also non-degradable.

The problem addressed by the present invention was to provide PVAc homopolymer dispersions for the described application with plasticizers which, on the one hand, would meet the wide-ranging requirement profile, but which on the other hand would be biologically safe and, in particular, degradable. The teaching in question is based on the knowledge that, basically, PVAc homopolymers are biologically safe and degradable even though degradation of this polymer is comparatively slow. The relevant literature is represented, for example, by H. Kastien et al. **"Der quantitative mikrobiologische Abbau von Lackkunstharzen und Polymerdispersionen (The Quantitative Microbiological Degradation of Paint-Grade Resins and Polymer Dispersions)", farbe + lack, Vol. 98, 7/1992, pages 505-508.** Accordingly, the problem addressed by the invention in the narrower sense is to provide hitherto unknown combinations of PVAc homopolymer dispersions and "biocompatible" plasticizers which would meet the wide-ranging technical requirement profile of soil stabilization, but which at the same time would as a whole undergo the natural degradation processes. Thereafter, the continuing stabilization of the surface layers in question can take place in known manner through plant growth

AUSTRALIAN PATENT OFFICE

processes occurring in the meantime, so that the initially applied and immediately effective synthetic stabilization of the surface layers is taken over by the now sufficiently advanced plant growth processes, the synthetic initial aid ultimately disappearing completely under the effect of natural degradation processes.

Although biologically acceptable plasticizers for PVAc dispersions are basically known per se, their use in accordance with the invention in such combinations for stabilizing surface layers of soil is not known. The relevant literature on plasticizer modification in PVAc polymers where they are used in the field of soil stabilization shows that it is not possible to make sufficiently reliable assertions on the fulfilment of the wide-ranging requirement profile in view of the change of plasticizer, cf. the Article by D.F. Anderson et al., **U.S. Nat. Techn. Inform. Serv., AD Rep., No. 732484, Avail. NTIS; Govt. Rep. Announce, (U.S.) 1972, 72 (1), 75 (Chemical Abstracts 76 (24):141689n).** Starting out from the basically satisfactory combination of PVAc homopolymer with dibutyl phthalate as plasticizer, attempts are made to establish universally satisfactory product properties using a number of other plasticizer components known per se. Even in regard to the basic requirement of adequate elasticity of the film, success is only achieved in the special case where plasticizers based on oligoethylene glycol derivatives are used. The other plasticizers investigated in the document cited above all lead to unacceptable embrittlement of the PVAc film.

The teaching according to the invention as described in the following is based on corresponding test results. From the basically large class of useful materials with plasticizer properties, particularly those based on natural substances, only three representatives have proved to be useful auxiliaries in the context of the

AUSTRALIAN PATENT OFFICE 13

problem addressed by the present invention.

Subject of the Invention

The present invention relates to the use of triesters of glycerol with lower aliphatic monocarboxylic acids, to the use of citric acid triesters with lower aliphatic monohydric alcohols and/or to the use of epoxidized triglycerides of at least partly olefinically unsaturated fatty acids as biologically degradable plasticizers in aqueous polyvinyl acetate dispersions where they are used for the surface stabilization of sand and/or soil.

Accordingly, there is provided according to a broad form of the invention a method of surface stabilization of sand and/or soil, which method comprises applying to the sand and/or soil an aqueous polyvinyl acetate dispersion containing at least one biodegradable plasticizer selected from a triester of glycerol with lower aliphatic monocarboxylic acids, a citric acid triester with lower aliphatic monohydric alcohols and/or an epoxidized triglyceride of at least partly olefinically unsaturated fatty acids.

Particulars of the Invention

Three types of low molecular weight plasticizers based on natural materials have proven to be suitable for satisfying the requirement profile according to the invention.

The first group comprises triesters of glycerol with lower aliphatic monocarboxylic acids. Corresponding glycerol triesters of aliphatic monocarboxylic acids containing 2 to 6 carbon atoms and, more particularly, 2 to 4 carbon atoms in the molecule are particularly suitable. A particularly important representative is triacetin. The studies on which the present invention is based have shown that even very small additions of triacetin to the PVAc homopolymer are sufficient to soften the PVAc film to an extent sufficient for the application according to the invention, so that the sand or soil formations impregnated with the mixture and solidified through drying of the water originally introduced do not become brittle and, hence, may be walked on for example.

The second group of plasticizers suitable for use in accordance with the invention is represented by citric

AUSTRALIAN PATENT OFFICE

acid triesters. The citric acid may be present as such and also in the form of the variant acylated at its hydroxyl group. Suitable ester-forming alcohols for the reaction with the carboxyl groups of the citric acid are, in particular, monohydric aliphatic alcohols containing 2 to 6 carbon atoms and preferably corresponding alcohols containing 2 to 4 carbon atoms. Both in this class of compounds and in the above-mentioned class of glycerol triesters with aliphatic monocarboxylic acids, the volatility and hence the boiling temperature of the plasticizer component can be influenced through the choice of the chain length of the particular monofunctional component used for the esterification process. In the case of the citric acid esters, further variation is possible through the chain length of the acyl group optionally attached to the hydroxyl group of the citric acid. Corresponding residues of monobasic, more particularly saturated, carboxylic acids containing 2 to 10 carbon atoms and, optionally, residues of corresponding acids containing an even larger number of carbon atoms are suitable for this purpose. The teaching according to the invention enables a possible loss of plasticizer under extreme conditions, for example in bright sunlight, and hence embrittlement of the films formed to be limited.

The third class of plasticizers in the context of the teaching according to the invention is represented by the epoxidized triglycerides of at least partly olefinically unsaturated fatty acids. The most important representatives of this class on practical and economic grounds are epoxidized rapeseed oil and epoxidized soybean oil which are marketed and proposed as commercial products for a variety applications, for example by the applicants. This sub-class of the plasticizers used in accordance with the invention clearly reflects the

AUSTRALIAN 13 PATENT OFFICE

selection character of the teaching according to the present invention: triglyceride esters of saturated and/or unsaturated fatty acids, more particularly corresponding triglycerides of natural origin which are present as oils under normal conditions, do not have an adequate plasticizing effect in admixture with PVAc homopolymers. Unexpectedly, the epoxidation of at least partly olefinically unsaturated triglycerides of this type and, more particularly, the epoxidation of rapeseed oil provides a plasticizer which meets the complex list of requirements, fulfils the conditions imposed here and, at the same time, undergoes natural degradation processes as a natural substance.

The quantity of plasticizer needed to meet the requirement profile in the dispersions used in accordance with the invention is limited. In general, quantities of plasticizer of around 1 to 15% by weight and, preferably, around 3 to 10% by weight (based on the approximately 50% by weight PVAc homopolymer dispersion) produce adequate results. Additions of around 5 to 8% by weight of plasticizer can be particularly important. An advantage of the teaching according to the invention which has already been discussed is clearly apparent here: a partial elimination of plasticizer occurring under extreme conditions, for example sunlight, does not have a directly adverse effect on the properties of the dried PVAc film in admixture with the stabilized soil. Even in the event of comparatively extensive elimination of plasticizer from the impregnation, the stabilized layer is still guaranteed adequate flexibility. The structural similarity of the plasticizer molecule to the structural unit of the PVAc homopolymer may possibly have a positive effect in this regard to the extent that the desired effect is maintained, even at low plasticizer concentrations, through the particularly deep penetration of the

AUSTRALIAN PATENT OFFICE

plasticizer into the polymer molecule.

The PVAc dispersions to be used in practice are the known aqueous preparations with PVAc solids contents of, for example, around 10 to 65% by weight and preferably in the range from about 35 to 60% by weight. Hitherto, aqueous PVAc dispersions have often been applied with corresponding solids contents of 50 to 60% by weight. In principle, use can also be made of this in the context of the teaching according to the invention.

In one particularly preferred embodiment, other additives of the aqueous impregnating and binding compositions selected in accordance with the invention are also biodegradable and hence biocompatible. This particular embodiment of the invention is characterized by the use of biodegradable protective colloids for stabilizing the aqueous PVAc dispersions. Suitable protective colloids are, on the one hand, polyvinyl alcohol and, on the other hand, starch and/or water-soluble starch derivatives; the starch may even be subjected to a partial reduction in molecular weight. However, where starch and/or water-soluble starch derivatives in particular are used as the protective colloids, the use of excessive quantities of these water-soluble components can endanger the stability of the film against erosion under the effect of rain and hence can lead to overly rapid degradation of the film. In a preferred embodiment of the invention, therefore, the quantities in which the protective colloids or rather emulsifiers are used are limited to such an extent that the PVAc film remains sufficiently resistant to the effects of weathering. The quantities in which the protective colloids or rather emulsifiers are normally used are at most around 5% by weight and, more particularly, in the range from about 0.5 to 3% by weight, based on the PVAc solids.

As for the rest, the technical elements developed in

AUSTRALIAN PATENT OFFICE

the relevant prior art for the formation of corresponding surface films may also be utilized in the context of the teaching according to the invention. For example, reference is made in this regard to the use of growth-promoting active substances, more particularly fertilizing auxiliaries, and/or to the use of preferably fine-particle solids, more particularly in the aqueous preparation of the impregnating composition. In the last-mentioned case, it is known that the prior art provides in particular for the use of fine-particle solids based on natural materials, such as sawdust, straw particles, cereal husks, coconut and/or flax fibers and the like, in order in this way to ensure the formation of local openings for further promoting plant growth without endangering the overall cohesion of the solidified layer. The soil-stabilizing aqueous active-substance preparation may be applied in known manner with plant seeds. However, the corresponding treatment of the soil may also take place independently of stabilization before or after application of the aqueous PVAc-based preparation according to the invention. The quantity of aqueous suspension applied is determined by a number of factors, including - purely by way of example - the penetrability of the upper soil layer, the desired objective and, in particular, the duration of the stabilizing effect and the weather-induced influences expected over the period for which sufficiently firm cohesion of the stabilized surface soil layers is to be guaranteed. In general, the depth of penetration of the aqueous PVAc dispersion into the soil will be at most a few centimeters, depths of penetration of around 0.5 to 3 cm and, more particularly, around 1 to 2 cm normally being sufficient. In many cases, however, soil stabilization to a depth of less than 1 cm is also entirely sufficient.

AUSTRALIAN PATENT OFFICE

Examples

Preparation Examples

Using a commercially available PVAc dispersion (approx. 50% by weight) - VP 4239/278 B (protective colloid polyvinyl alcohol), a product of Cordes - mixtures with 5% by weight and 10% by weight - based on the aqueous dispersion - of the plasticizers listed below are prepared as follows:

Preparation of the dispersions:

The plasticizer is added to the dispersion with stirring at room temperature, followed by stirring for 10 minutes.

Condition: IKA stirrer with paddle stirrer, r.p.m. = 900 min^{-1}

The plasticizer-containing dispersions are applied as films and the dried films are evaluated.

Production of the films:

The dispersion/plasticizer mixture is knife-coated onto a Teflon plate (in the case of the glycerol-containing mixtures, the film was applied to polyethylene). The films are dried at room temperature.

Condition: coating knife = 400 µm
Drying time: 4 - 6 h

The following plasticizers were used:

1) triacetin
2) acetyl butyl ricinoleate
3) rapeseed oil fatty acid methyl ester
4) ricinene fatty acid methyl ester
5) glycerol
6) triethyl citrate

AUSTRALIAN PATENT OFFICE

7) acetyl triethyl citrate
8) tributyl citrate
9) rapeseed oil
10) rapeseed oil ethylhexyl ester
11) epoxidized soybean oil (commercial product EDENOR D 81).

The films formed with these plasticizers are evaluated for flexibility, solubility in water and cohesion. The dispersion mixture used is tested for stability and homogeneity after standing for more than 14 days.

Useful results in the context of the teaching according to the invention are only obtained where the following plasticizers are used:

1) triacetin
6) triethyl citrate
7) acetyl triethyl citrate
8) tributyl citrate
11) epoxidized soybean oil.

The stability and homogeneity of the dispersion mixtures according to the invention after more than 14 days are very good both where 5% by weight of plasticizer and where 10% by weight of plasticizer is added.

In no case is the dried film soluble in water. Where the plasticizers are added in quantities of 10% by weight, the films are all evaluated as "very flexible". They are also "very flexible" in the case of acetyl triethyl citrate added in a quantity of 5% by weight. In every other case, the addition of 5% by weight produces a flexibility evaluation of "flexible".

The cohesion of the films is very good in every case. Where 10% by weight of plasticizer is added and, in the case of acetyl triethyl citrate, even where 5% by

AUSTRALIAN PATENT OFFICE

weight is added, the film can be forcibly stretched before tearing. The addition of 5% by weight of the other plasticizers produces such cohesion that the film only tears under considerable force.

Sand layers can be stabilized with the aqueous PVAc dispersions containing plasticizers corresponding to the definition according to the invention in such a way that they are resistant to weathering and can be walked on.

Application Examples

1) Stabilization of sand surfaces

The above-mentioned PVAc dispersion VP4239/278B containing various plasticizers added in various quantities was used in surface stabilization tests on sand samples. PVAc dispersions with the following additions were used:

1.1) no added plasticizer (comparison test)
1.2) 2% by weight of triacetin
1.3) 5% by weight of triacetin
1.4) 10% by weight of triacetin
1.5) 10% by weight of epoxidized soybean oil (EDENOR D81)
1.6) 10% by weight of dibutyl phthalate (comparison test).

The tests were carried out as follows:

The surfaces of identical sand samples were treated with identical quantities of 10% by weight solutions of the dispersions mentioned above. The particular hardening time required was then determined at ambient temperature (around 20 to 25°C). Result: no significant differences between the individual samples were observed. All the samples required a hardening time of more than 16 hours.

In addition, the water absorption capacity and

AUSTRALIAN PATENT OFFICE J 3

surface elasticity of the hardened samples were investigated and visually compared. Once again, there were no significant differences between the individual samples.

The test described above were repeated using a 5% by weight solution of the above-mentioned dispersions. So far as the particular surface hardness of the individual samples was concerned, those samples which had been obtained with dispersions containing added triacetin showed generally better behavior, i.e. the overall stabilization of the sand surfaces was stronger. Slight differences were observed in the surface elasticity of the samples obtained with formulations 1.2 and 1.3 (2% and 5% by weight of added triacetin) and the sample obtained with formulation 1.4 (10% by weight of added triacetin).

2) Testing of weather influences on stabilized sand surfaces

For these tests, the above-mentioned PVAc dispersions with an addition of 5% by weight of triacetin were used in the form of 10% by weight solutions. Metal trays filled with 1500 g of sand in a layer thickness of around 3 to 4 cm were used as the test surfaces. This corresponds to a surface area of around 740 cm^2. The PVAc dispersion was applied to the sand surfaces with a brush. The quantity used was around 150 g and thus corresponded to around 2000 g of starting dispersion per square meter of sand surface. After a hardening time of 16 hours at ambient temperature (20 to 25°C), the sand samples thus treated were stored under the following conditions:

2.1) 4 days at ambient temperature in the laboratory,
2.2) 12 days outdoors with artificial watering (the sand was half-mixed with topsoil)
2.3) 9 days outdoor with rainy days

AUSTRALIAN PATENT OFFICE

2.4) 4 days in a conditioning cabinet with ambient air at 10°C,

2.5) 4 days in a drying cabinet without ambient air at 40°C.

Result: the sand surface obtained in test 2.1 was resilient, i.e. relatively elastic, under relatively strong pressure. The samples stored outdoors in tests 2.2 and 2.3 did not show any significant differences in hardness at the end of the test despite the effect of rain, artificial watering and slight inclination during storage. The hardening of the sand surfaces was generally regarded as very good. In test 2.4, uneven hardening of the sand surface was observed with areas where the surface had not hardened at all. This effect is attributable to the ambient air prevailing in the conditioning cabinet used in this test because it induces extremely rapid drying of the sand surface. By contrast, the sample in test 2.5 (no ambient air) did not show any differences in hardness over the sand surface. On the contrary, the result obtained corresponded to the results obtained in tests 2.2 and 2.3.

3) Other practical tests

The above-mentioned PVAc dispersion with an addition of 5% by weight of triacetin was again used in the form of a 10% by weight solution for these tests.

3.1) Grassing

Sand samples were prepared as in Example 2 but were half-mixed with topsoil (ratio of sand to topsoil 1:1). The sand samples were treated with a PVAc dispersion additionally containing grass seeds. Sand samples containing grass seeds which had not been treated with PVAc dispersion were used as reference. Result: no

AUSTRALIAN PATENT OFFICE 13

significant differences were observed in regard to grass growth, growth density and grass color.

3.2) Vinyl acetate content in eluates

A filter nutsche was filled with a layer of sand which was then treated with PVAc dispersion. The hardening time was 16 hours at ambient temperature (20 to 25°C). A defined quantity of water was then poured onto the layer of sand every day for 10 days and the respective eluate samples (samples 1 to 10) were collected. An eluate which had been obtained from a corresponding untreated layer of sand was used as reference. Sample 9 (i.e. the eluate sample for day 9) was analyzed by head space GC, being spiked with vinyl acetate standard for quantification. The vinyl acetate content determined in this sample was less than 1 ppm.

3.3) COD and TOC values in eluates

The chemical oxygen demand (COD values) and total organic carbon (TOC values) were determined in some of the eluates described above. The COD values were determined in accordance with DIN 38409 H41/1 while the TOC values were determined in accordance with DIN 38409 H3. The eluate samples were stored in a refrigerator (4°C) pending evaluation. Result:

	COD [mg/l]	TOC [mg/l]
Sample 1	92.6	31.4
Sample 10	4.0*	2.7
Samples 2 to 8 (average value of the combined samples)	-	1.8
Reference value 1	4.0*	3.8
Reference value 10	1.0*	1.3

* These values are in the range of error of the methods.

AUSTRALIAN PATENT OFFICE

The values determined with sample 1 are clearly attributable to the fact that adequate hardening had still not occurred. However, they are by no means critical values. Overall, the values obtained may be described as very positive. In view of this, the COD value of combined samples 2 to 8 was not determined.

3.4) Outdoor tests

For the outdoor tests, areas of around 30 m² with an inclination of around 60° of loose topsoil and loose sand were sprayed with a PVAc dispersion diluted in a ratio of 1:8 (5% by weight addition of triacetin). The application of around 2 kg of dispersion per square meter was made towards 3.00 pm on a November afternoon. The evaluation was carried out after solidification on the following day, again towards 3.00 pm. Result: despite unfavorable weather conditions (ground mist in the morning, night temperatures around 4 to 6°C), excellent soil stabilization was obtained and, even after a few days, was still the same.

AUSTRALIAN PATENT OFFICE

The claims defining the invention are as follows:

1. A method of surface stabilization of sand and/or soil, which method comprises applying to the sand and/or soil an aqueous polyvinyl acetate dispersion containing at least one biodegradable plasticizer selected from a triester of glycerol with lower aliphatic monocarboxylic acids, a citric acid triester with lower aliphatic monohydric alcohols and/or an epoxidized triglyceride of at least partly olefinically unsaturated fatty acids.

2. A method according to claim 1, wherein the aliphatic monocarboxylic acids contain 2 to 6 carbon atoms.

3. A method according to claim 2, wherein the aliphatic monocarboxylic acids contain 2 to 4 carbon atoms.

4. A method according to claim 3, wherein the glycerol triester of aliphatic monocarboxylic acids is triacetin.

5. A method according to any one of claims 1 to 4, wherein the aliphatic monohydric alcohols contain 2 to 6 carbon atoms.

6. A method according to claim 5, wherein the aliphatic monohydric alcohols contain 2 to 4 carbon atoms.

7. A method according to any one of claims 1 to 6, wherein the epoxidized triglyceride of at least partly olefinically unsaturated fatty acids is epoxidized rapeseed oil and/or epoxidized soybean oil.

8. A method according to any one of claims 1 to 7, wherein the plasticizer is added to the aqueous polyvinyl acetate dispersion and is present in a quantity of around 1 to 15% by weight based on approximately 50% by weight aqueous polyvinyl acetate dispersion.

9. A method according to claim 8, wherein the plasticizer is added in quantities of around 3 to 10% by weight.

10. A method according to any one of claims 1 to 9, wherein the aqueous polyvinyl acetate dispersion has a solids content of around 10 to 65% by weight.

11. A method according to claim 10, wherein aqueous polyvinyl acetate dispersion has solids content of around 35 to 60% by weight.

12. A method according to any one of claims 1 to 11, wherein the aqueous polyvinyl acetate dispersion is stabilized with at least one biodegradable protective colloid.

13. A method according to claim 12, wherein the biodegradable protective colloid is a polyvinyl alcohol and/or starch and/or water-soluble starch derivative.

14. A method according to claim 12 or 13, wherein the quantity of biodegradable protective colloid is limited to such an extent that the polyvinyl acetate coating on the soil remains sufficiently resistant to the effects of weather.

15. A method according to claim 14, wherein the biodegradable protective colloid is used in a quantity of up to about 5% by weight based on polyvinyl acetate solids.

AUSTRALIAN PATENT OFFICE A 3

16. A method according to claim 15, wherein the biodegradable protective colloid is used in a quantity of about 0.5 to 3% by weight based on polyvinyl acetate solids.

17. A method of surface stabilization of sand and/or soil, which method comprises applying to the sand and/or soil a polyvinyl acetate dispersion of any one of the Preparation Examples in an amount which stabilizes the surface of the sand and/or soil.

Dated 11 March, 1997
Henkel Kommanditgesellschaft auf Aktien
Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON





INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/02284

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K17/20 E21B43/02 C09K17/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB,A,906 470 (W.A. SCHOLTEN'S CHEMISCHE FABRIEKEN) 19 September 1962 see page 1, line 48 - line 67 see page 2, line 2 - line 17 see page 2, line 36 - line 48 see page 2, line 75 - line 97	1,7
Y	US,A,4 072 020 (REVERTEX) 7 February 1978 cited in the application see column 1, line 19 - line 36 see claim 1; examples 3,5	1,7
Y	US,A,3 887 506 (R.L.HEWITT) 3 June 1975 cited in the application see column 2, line 3 - line 22 see column 3, line 39 - line 46	1,7

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 1994	19. 10. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Boulon, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Intern. onal Application No
PCT/EP 94/02284

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 82-06810E & JP,A,56 161 462 (KURARAY) 11 December 1981 see abstract ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 004, no. 042 (C-005) 3 April 1980 & JP,A,55 016 074 (KYOKADO ENG.) 4 February 1980 see abstract ---	1,2
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 77-33585Y & JP,A,52 040 540 (NIPPON SYNTH. CHEM. K.K) 29 March 1977 see abstract -----	1

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. .onal Application No
PCT/EP 94/02284

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-906470		NONE	
US-A-4072020	07-02-78	NONE	
US-A-3887506	03-06-75	NONE	

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 94/02284

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 6 C09K17/20 E21B43/02 C09K17/14

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 6 C09K E21B

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	GB,A,906 470 (W.A. SCHOLTEN'S CHEMISCHE FABRIEKEN) 19. September 1962 siehe Seite 1, Zeile 48 - Zeile 67 siehe Seite 2, Zeile 2 - Zeile 17 siehe Seite 2, Zeile 36 - Zeile 48 siehe Seite 2, Zeile 75 - Zeile 97 ---	1,7
Y	US,A,4 072 020 (REVERTEX) 7. Februar 1978 in der Anmeldung erwähnt siehe Spalte 1, Zeile 19 - Zeile 36 siehe Anspruch 1; Beispiele 3,5 ---	1,7
Y	US,A,3 887 506 (R.L.HEWITT) 3. Juni 1975 in der Anmeldung erwähnt siehe Spalte 2, Zeile 3 - Zeile 22 siehe Spalte 3, Zeile 39 - Zeile 46 --- -/--	1,7

[X] Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

[X] Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :
"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist
"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist
"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)
"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht
"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist
"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist
"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden
"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist
"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

1

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
4. Oktober 1994	19. 10. 94
Name und Postanschrift der Internationale Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	**Bevollmächtigter Bediensteter** Boulon, A

Formblatt PCT/ISA/210 (Blatt 2) (Juli 1992)

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 94/02284

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 82-06810E & JP,A,56 161 462 (KURARAY) 11. Dezember 1981 siehe Zusammenfassung ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 004, no. 042 (C-005) 3. April 1980 & JP,A,55 016 074 (KYOKADO ENG.) 4. Februar 1980 siehe Zusammenfassung ---	1,2
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 77-33585Y & JP,A,52 040 540 (NIPPON SYNTH. CHEM. K.K) 29. März 1977 siehe Zusammenfassung -----	1

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen
PCT/EP 94/02284

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
GB-A-906470		KEINE	
US-A-4072020	07-02-78	KEINE	
US-A-3887506	03-06-75	KEINE	