CONVENTION

AUSTRALIA

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APPLICATION FOR A STANDARD PATENT

Grace GmbH
Erlengang 31, D-2000 Norderstedt, FEDERAL REPUBLIC OF GERMANY

621506

hereby applies for the grant of a standard patent for an invention entitled:

LEAD/SULPHURIC ACID-ACCUMULATOR, SEPARATOR FOR LEAD/SULPHURIC ACID ACCUMULATORS AND PROCESS TO REDUCE THE FORMATION OF COLORED DEPOSITS IN A LEAD/SULPHURIC ACID ACCUMULATOR

which is described in the accompanying complete specification.

Details of basic application(s):-
P39 28 468.9 FEDERAL REPUBLIC OF GERMANY 29 August 1989

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DATED this TENTH day of AUGUST 1990

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By: David B Fitzpatrick

Our Ref : 184616
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Case 3221

An Australian patent application must be supported by a declaration before it can be allowed. The declaration may be filed with the application or subsequently.

This comprehensive form is suitable for convention or non-convention applications by individuals or corporate bodies. For non-convention applications omit paragraphs 3 and 4. *Where applicant is a body corporate take special care that the declarant specified at clause (e) is a fully authorized officer such as Director, President, or Secretary.

** If applicable, take special care in completing clause (g) e.g. by specifying "Applicant is the assignee of the invention from the actual inventor".

Note: Any alterations to your insertions must be initialled in the margin by the declarant(s).

AUSTRALIA
Patent Declaration

Suitable any application

No legalization or other witness required

Filable after application

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DECLARATION FOR A PATENT APPLICATION

▼ INSTRUCTIONS
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) Convention application made by (b)

Grace GmbH

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(s) for a patent (c) for an invention entitled (d) "Lead/Sulphuric Acid-Accumulator, Separator for Lead/Sulphuric Acid Accumulators and Process to Reduce the Formation of Colored Deposits in a Lead/Sulphuric Acid Accumulator"

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/We (e) Rudolf Hartmann, General Manager, Grace GmbH, Erlengang 31, D-2000 Norderstedt, West Germany

do solemnly and sincerely declare as follows:

~~1. I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant~~(s)~~.

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f)
Hellmut Bünsch, Saseler Mühlenweg 47 a, 2000 Hamburg 65, W.Germany
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Frank Otto Theubert, Heinrich-Loennies-Strasse 64, 2000 Norderstedt, W. Germany

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant~~(s)~~ is/~~are~~ entitled to make the application are as follows:

(g)
Applicant is the assignee of the invention from the actual inventors

(Note: Paragraphs 3 and 4 apply only to Convention applications)

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application~~(s)~~ for patent or similar protection on which the application is based is/~~are~~ identified by **country, filing date, and basic applicant~~(s)~~** as follows:

(h)
West Germany
August 29, 1989
Grace GmbH

4. The basic application~~(s)~~ referred to in paragraph 3 hereof was/~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing

Declared at (k) Nordersted, West Germany

(12) PATENT ABRIDGMENT (11) Document No. AU-B-60957/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 621506

(54) Title
LEAD/SULPHURIC ACID-ACCUMULATOR, SEPARATOR FOR LEAD/SULPHURIC ACID ACCUMULATORS AND PROCESS TO REDUCE THE FORMATION OF COLORED DEPOSITS IN A LEAD/SULPHURIC ACID ACCUMULATOR

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(56) Prior Art Documents
AU 27076/88 H01M 2/16
AU 79762/87 H01M 2/16

(57) Claim

1. A lead/sulphuric acid accumulator with at least one separator made from filled poly-olefin, characterized in that the separator contains as ~~the~~ a plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content of $\leq$ 2000 ppm and a polar part of $\leq$ 1.0 %.

11. A separator of filled poly-olefin for lead/sulphuric acid accumulators, characterized in that it contains as ~~the~~ a plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content of $\leq$ 2000 ppm and a polar part of $\leq$ 1.0%.

21. A process to reduce the formation of coloured deposits in a lead/sulphuric acid accumulator with at least one separator of filled poly-olefin, characterized in that in the accumulator separators according to any one of claims 11 to 20 are used.

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COMPLETE SPECIFICATION
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Related Art:

Applicant(s):

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Address for Service is:

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Complete Specification for the invention entitled:

LEAD/SULPHURIC ACID-ACCUMULATOR, SEPARATOR FOR LEAD/SULPHURIC ACID ACCUMULATORS AND PROCESS TO REDUCE THE FORMATION OF COLORED DEPOSITS IN A LEAD/SULPHURIC ACID ACCUMULATOR

Our Ref : 18[illegible]516
POF Code: 90766/1236

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

6006

Lead/sulphuric acid-accumulator, Separator for lead/sulphuric acid accumulators and process to reduce the formation of coloured deposits in a lead/sulphuric acid accumulator

Lead/sulphuric acid-accumulators (for the sake of brevity referred to below as lead accumulators) contain to an ever increasing extent separators made from filled poly-olefins. These separators are micro-porous separators, the composition and manufacture of which is known from the prior art (see, for example, DE-PS 1 267 423, DE-PS 1 298 712, DE-AS 1 496 123, DE-OS 35 45 615, DE-PS 35 40 718, DE-PS 36 17 318, DE-OS 30 04 659, GB-A 2,027,637, US-PS 4,024,323 and US-PS 4,237,083).

In contrast to separators based on impregnated cellulose paper, PVC or phenol-formaldehyde-resins, separators made from filled poly-olefins offer various advantages. On the one hand as a result of their favourable range of properties, the life duration and performance of lead accumulators can be improved, and on the other hand there are also advantages in the manufacture of the accumulator. The high flexibility of the separators made from filled poly-olefins allows fully automatic enveloping of lead plates and final sealing of the side edges, with the result that the lead plates are protected in a separator pocket, closed on three sides.

However, in the use of separators made from filled poly-olefins in lead accumulators undesired processes are also observed.

Through the interaction of the applied current, the constituents of the lead plates, the constituents of the battery acid and the constituents of the filled poly-olefin separators, substances or substance mixtures form in the lead accumulator, which as a result of their low specific weight rise to the surface of the battery acid and there form mostly coloured and often also adhesive agglomerates, which tend to be deposited on the contact surfaces between the accumulator acid and the accumulator constituents, for example on the housing. Gases released in the charging process rise in bubbles in the acid, bursting on the surface of the acid thereby throwing acid and deposits upwards, which results in the cover, the cover opening, the cover-fastening possibly placed on it and the outside of the accumulator housing being covered with it.

Housings for lead accumulators consist, for example, of polypropylene,

methacrylate or polystyrene and are therefore transparent or totally clear. Coloured deposits forming when the lead accumulator is in use deposit themselves on the inside of the containers and are therefore visible from the outside. As the deposits themselves are not transparent, an exact assessment of the acid level in the lead accumulator is prevented, thereby making the regular inspection and adjustment of the acid level more difficult. If insufficient water is added, the concentration of the accumulator acid increases. At the same time the acid level in the accumulator can possibly sink so far that the lead plates partly protrude out of the acid and dry out.

Lead accumulators which, for example, are used for driving vehicles, are often fitted with a valve system for automatic water-addition. These lead accumulators are regularly connected to a water reserve tank via the valve system. When in proper working order the valve system ensures that a certain level of liquid is maintained in the lead accumulator. However, if this type of lead accumulator contains separators made of filled poly-olefins, then as described above, deposits form which can cause the water-addition system to be incapable of functioning. Consequently no water is added, and the acid level in the accumulator falls.

Many lead accumulators are fitted with gassing openings made from porous materials, which facilitate an unhindered escape of the gases formed but are intended to prevent oxyhydrogen explosions by keeping away sparks. If this type of lead accumulator contains the filled poly-olefin separators described above, deposits can form when the lead accumulator is in use, as described, which can obstruct the de-gassing openings and thus make them impermeable to gases.

In view of the problems described above, the basis of the objective of the invention is to reduce the quantity of coloured, mostly dark and frequently adhesive deposits formed in lead accumulators with separators made from filled poly-olefins during formation and use.

To achieve this objective a lead/sulphuric acid accumulator with at least one separator made from filled poly-olefins is proposed which is characterized in that the separator contains as the plasticizer a process oil with an aromatic hydrocarbon content hereinafter C_A value of $\leq$ 6%, a sulphur content $\leq$ 2000 ppm and a polar part of $\leq$ 1.0 %.

In addition, the subject of the invention is a separator made from filled poly-olefin for lead/sulphuric acid accumulators, which is characterized in that it contains as the plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content $\leq$ 2000 ppm and a polar fraction of $\leq$ 1.0 %.

Finally, the subject of the invention is a process for reducing the formation of coloured, mostly dark and frequently adhesive deposits in a lead/sulphuric acid accumulator with at least one separator made from filled poly-olefin, characterized in that separators are used in the accumulator which contain as the plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content $\leq$ 2000 ppm and a polar part of $\leq$ 1.0 %.

It was surprisingly found that a decisive reduction in the aforementioned deposits can be achieved by the use of process oils as plasticizers for separators made from filled poly-olefin, if the oils

have a C_A value according to DIN 51378 (without sulphur correction) of $\leq$ 6%, a total sulphur content measurable according to DIN 51400 of $\leq$ 2000 ppm and a polar part according to ASTM D 20007-75 (polar compounds in % by weight) of $\leq$ 1.0%.

The mineral oils effective according to the invention are distinguished by the fact that they simultaneously meet the conditions $C_A \leq 6\%$, total sulphur content $\leq$ 2000 ppm and polar part $\leq$ 1.0 %. By their nature these oils can be not only relatively naphthenic, or naphthenic but also paraffinic, with the viscosity/density constant serving for classification (Ullmans Encyclopaedie der technischen Chemie, Verlag Chemie 1981, 4th. edition, Volume 20, page 616). Relatively naphthenic oils with a viscosity/density constant of 0.820 - 0.849 are most preferred, while paraffinic oils are least preferred. In the latter the C_A value should be greater than 0.1 %, preferably greater than 0.5% and particularly greater than 1 % and the sulphur content should be greater than 100 ppm. Aromatic oils basically do not fulfil the condition $C_A \leq 6$ % and S $\leq$ 2000 ppm and are therefore not considered for use according to the invention.

The process oils effective according to the invention preferably have a C_A value of $\leq$ 5%, and more preferred $\leq$ 3% and particularly $\leq$ 2%. The sulphur content of the process oils effective according to the invention is preferably $\leq$ 1000 ppm, more preferred $\leq$ 500 ppm and particularly $\leq$ 100 ppm. The polar part in the process oils effective according to the invention is preferably $\leq$ 0.7 %, more preferred $\leq$ 0.5 % and particularly $\leq$ 0.3 %.

The plasticizer content of the separator according to the invention is

within the normal boundaries. The plasticizer quantity referred to the separator weight is usually 1 to 40 % by weight. Preferred plasticizer contents are 5 to 25 % by weight and particularly 10 to 15 % by weight. In addition to the highly refined process oils used according to the invention other usual plasticizers can also be used (see below).

Except for the process oils contained as plasticizers in the separators, the accumulator according to the invention is a usual lead/sulphuric acid accumulator with conventional electrodes and sulphuric acid as the electrolyte.

As already described in the prior art mentioned above, filled polyolefin separators mainly contain polyethylene, where within the framework of the invention polyethylene of ultra-high molecular weight is preferred (average molecular weight of at least 1 000 000). However, polypropylene, polybutene, polystyrene, ethylene-propylene co-polymers, ethylene-hexylene co-polymers, ethylene-butene co-polymers, propylene-butene co-polymers, ethylene-propylene-butene co-polymers, and co-polymers of ethylene or propylene with an ethylene unsaturated mono-carbonic acid, such as acrylic acid, methacrylic acid or mixtures of these are suitable. The prior art mentioned at the beginning can also be referred to with regard to fillers. A preferred filler according to the invention is SiO_2.

Apart from the main constituents mentioned above the separators can also contain further usual constituents such as carbon black, anti-oxidants, lubricants, other fillers such as, for example, talcum etc. and possibly also other polymers in more or less minor quantities.

The materials forming the separators are carefully mixed in the usual manner and then formed, while heating, into a long length of material (generally known as foil). The plasticizer is then extracted from this with an organic solvent in order to achieve the desired porosity. Finally, the separator material is cut into the separator sheets. The surfaces of the separators can be flat, ribbed or formed in other arbitrary ways.

The process oil used according to the invention can be introduced into the separator by adding it to the starting mixture and extracting the foil at a certain residual oil content. Another possibility is to use a plasticizer according to the invention or another plasticizer in the starting mixture, to extract this plasticizer completely or incompletely and to coat the free-lying surfaces of the battery separator with the desired quantity of the oil suitable according to the invention. For this the separator can, for example, be immersed in an oil/solvent solution and the solvent removed or the oil can be rolled or sprayed, either alone or with a diluent, on to the separator.

The process of complete extraction and refilling by immersion in an oil/solvent solution is termed "re-equilibration" in the following.

In addition to other substances in the prior art many different types of oil are used or proposed as plasticizers. However, the aromatic hydrocarbon part, the sulphur content and the polar part are either not discussed or the proposed oils do not fulfil the conditions given above. For example, aromatic oils are proposed in DE-OS 30 04 659, while the Shellflex 411 named in US-PS 3 351 495 and DE-AS 1 496 123 has a C_A value of 8 % and the Shellflex 412 named in US-PS 4 024 323

has a polar part of 1.3%.

The use of the process oils suitable according to the invention as plasticizers has also not previously been proposed in connection with the formation of the coloured, mostly dark and often adhesive deposits observed when filled poly-olefin separators are used. This is extremely surprising in view of the severity of the problem of the formation of such deposits, known as black scum or grey scum, and the widespread use of process oils as plasticizers in separators, and shows that experts have obviously not taken the aromatic hydrocarbon part, the sulphur part and the polar part of the process oils used as plasticizers into consideration in solving the black scum problem.

The invention will be explained below by means of examples. Accumulator tests were carried out to evaluate the effectiveness of process oils as plasticizers. The sample accumulators used in these tests consisted of cells which each had 5 positive and 4 negative plates, antimony content 2.5 % by weight, with a total capacity of 36 Ah/cell. If not otherwise indicated the negative plates were separated with separator pockets of filled poly-olefins (total thickness 1.0 mm), which had been produced according to the process in US-PS 3 351 495. The electrolyte was sulphuric acid in an amount of 400 ml/cell.

After the tests had been carried out, the cells were opened and the amount of coloured deposit on the cell boxes, cell covers and stoppers was evaluated by several persons, with 20 points given in the marking system for the heaviest deposits and 1 point given for the least deposits. An average was calculated from all the evaluations.

Example 1

Separators made of filled polyethylene were extracted with hexane to constant weight and thus completely freed of oil. They were then re-equilibrated in the manner described above with the oils listed in Table 1. Accumulators according to the above description, which were each provided with four separator pockets, were subjected to the same electrical test. They were then opened and evaluated as described above. The results are also reproduced in Table 1.

Example 2

Commercial separators presumably manufactured according to US-PS 4,024,323 (indicated as "commercial product" in Table 2) were re-equilibrated with the oils listed in Table 2 just as in Example 1. These separators were subjected, as in Example 1, to an electrical test to evaluate the amount of deposits. For comparison purposes both separators of filled polyethylene, manufactured with Shellflex 411 (oil 4) by extrusion and extraction to the desired residual residual oil content (indicated as "original" in Table 2), and re-equilibrated separators of filled polyethylene, were subjected in parallel to this procedure.

Table 1

Oil	Oil type	C_A (%)	Sulphur content (ppm)	Polar part (%)	Oil content (%) of the separators	Amount of deposits
(1)	aromatic	43	40,000	> 4.0	12.3	17
(2)	naphthenic	11	800	0.3	13.2	14
(3)	paraffinic	8	8,000	> 1.0	11.7	13
(4)	rel. naphthenic	8	500	1.3	11.9	13
(5)	rel. naphthenic	8	500	0.3	11.2	13
(6)	paraffinic	2	2,300	0.9	12.5	11
(7)	paraffinic	4	4,000	1.0	11.9	10
(8)	rel. naphthenic	4	1,000	1.3	12.3	10
(9)	rel. naphthenic	5	400	0.2	12.0	4
(10)	rel. naphthenic	5	100	0.2	12.6	3
(11)	paraffinic	3	1,000	0.1	11.8	3
(12)	paraffinic	2	1,000	0.2	12.3	3

Table 2

	Separator	Oil [1]	Manner of oil application	Amount of deposit
(1)	commercial product	(4)	re-equilibration	13
(2)	commercial product	(10)	re-equilibration	3
(3)	filled PE[2]	(4)	re-equilibration	12
(4)	filled PE[2]	(10)	re-equilibration	2
(5)	filled PE[2]	(4)	original	13

1) Oil data see table 1 under the appropriate number

2) Filled PE = filled polyethylene

The claims defining the invention are as follows:

1. A lead/sulphuric acid accumulator with at least one separator made from filled poly-olefin, characterized in that the separator contains as ~~the~~ a plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content of $\leq$ 2000 ppm and a polar part of $\leq$ 1.0 %.

2. An accumulator according to claim 1, characterized in that the C_A value of the process oil is $\leq$ 5%, preferably $\leq$ 3% and particularly $\leq$ 2%.

3. An accumulator according to claim 1 or 2, characterized in that the sulphur content of the process oil is $\leq$ 1000 ppm, preferably $\leq$ 500 ppm and particularly $\leq$ 100 ppm.

4. An accumulator according to any one of claims 1 to 3, characterized in that the polar part of the process oil is $\leq$ 0.7%, preferably $\leq$ 0.5% and particularly 0.3%.

5. An accumulator according to any one of claims 1 to 4, characterized in that the process oil is a naphthenic and preferably a relatively naphthenic oil.

6. An accumulator according to any one of claims 1 to 4, characterized in that the process oil is a paraffinic oil and has a C_A value of more than 0.1%, preferably more than 0.5% and particularly more than 1%.

7. An accumulator according to claim 6, characterized in that the sulphur content of the process oil is greater than 100 ppm.

8. An accumulator according to any one of claims 1 to 7, characterized in that the separator contains 1 to 40% by weight, preferably 5 to 25% by weight, and particularly 10 to 15% by weight of process oil as plasticizer.

9. An accumulator according to any one of claims 1 to 8, characterized in that the separator also contains one or more usual plasticizers.

10. An accumulator according to any one of claims 1 to 9, characterized in that the separator consists of filled polyethylene, particularly polyethylene of ultra-high molecular weight and is essentially filled with SiO_2.

11. A separator of filled poly-olefin for lead/sulphuric

acid accumulators, characterized in that it contains as ~~the~~ a plasticizer a process oil with a C_A value of $\leq$ 6%, a sulphur content of $\leq$ 2000 ppm and a polar part of $\leq$ 1.0%.

12. A separator according to claim 11, characterized in that the process oil has a C_A value of $\leq$ 5%, preferably $\leq$ 3% and particularly $\leq$ 2%.

13. A separator according to claim 11 or 12, characterized in that the sulphur content of the process oil is $\leq$ 1000 ppm, preferably $\leq$ 500 ppm and particularly $\leq$ 100 ppm.

14. A separator according to any one of claims 11 to 13, characterized in that the polar part of the process oil is $\leq$ 0.7%, preferably $\leq$ 0.5% and particularly $\leq$ 0.3%.

15. A separator according to any one of claims 11 to 14, characterized in that the process oil is a naphthenic and preferably a relatively naphthenic oil.

16. A separator according to any one of claims 11 to 14, characterized in that the process oil is a paraffinic oil and has a C_A value of more than 0.1%, preferably more than 0.5% and particularly more than 1%.

17. A separator according to claim 16, characterized in that the sulphur content of the process oil is greater than 100 ppm.

18. A separator according to any one of claims 11 to 17, characterized in that it contains 1 to 40% by weight, preferably 5 to 25% by weight and particularly 10 to 15% by weight of plasticizer.

19. A separator according to any one of claims 11 to 18, characterized in that it contains in addition one or more usual plasticizers.

20. A separator according to any one of claims 11 to 19, characterized in that it consists of filled polyethylene, particularly polyethylene of ultra-high molecular weight and is essentially filled with SiO_2 and plasticizer.

21. A process to reduce the formation of coloured deposits in a lead/sulphuric acid accumulator with at least one separator of filled poly-olefin, characterized in that in the accumulator separators according to any one

of claims 11 to 20 are used.

22. An accumulator substantially as hereinbefore described with reference to any one of the examples.

23. A separator substantially as hereinbefore described with reference to any one of the examples.

24. A process substantially as hereinbefore described with reference to any one of the examples.

DATED: 8th August 1990

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