(54) Title: SEPARATOR WITH IMPROVED TENSILE STRENGTH FOR STARVED ELECTROLYTE LEAD/ACID BATTERY

(57) Abstract

Compositions and papers made therefrom useful as separator materials in starved electrolyte lead/acid batteries described. The compositions comprise a mixture of 15 percent to 75 percent by weight of perlite, 20 percent to 70 percent by weight of glass fibers, and 5 percent to 20 percent by weight of acid-insoluble thermoplastic fibers, the latter preferably in the form of staple fibers. The glass fibers have diameters in the range of from 0.3 to 1.0 micrometers while the perlite has particle sizes in the range of from about 30 to about 100 micrometers.
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SEPARATOR WITH IMPROVED TENSILE STRENGTH
FOR STARVED ELECTROLYTE LEAD/ACID BATTERY

Technical Field

The invention herein relates to lead/acid electric storage batteries. More particularly it relates to separators for such batteries.

Background of the Prior Art

Recently efficient maintenance-free rechargeable sealed lead/acid storage batteries utilizing a "starved electrolyte" concept have been introduced commercially. Various aspects of batteries of this type are disclosed in a number of patents, most notably U.S. Patent No. 3,862,861. Such batteries normally utilize as separators materials such as microporous rubber, polyvinyl chloride, polyolefins, phenolic resin impregnated paper or (preferably) glass paper made from microfiber diameter, unwoven, short staple glass fibers. These batteries, while useful in a wide variety of applications, have been severely limited in the practical sizes which can be commercially utilized because of the high cost of these batteries per unit of energy density. Thus, while cells of the common C, D, "beer can" and similar sizes are practical for some purposes commercially, larger sizes such as the typical automotive battery size are far too costly for commercial practicality. Similarly, the high unit density cost of even the smaller size batteries have restricted these types of batteries to high value end uses such as in spacecraft and emergency equipment, effectively eliminating the batteries from the fields of conventional consumer use such as flashlights, radios and the like.

In these types of batteries a very high proportion of the cost of battery materials lies in the cost of the separator. The preferred microfiber glass paper separators are extremely costly. In the past, however, attempts to substitute lower cost materials have
led to battery structures with significantly poorer electrical characteristics.

Recently, a low cost high efficiency battery separator composition for starved electrolyte batteries has been developed and described and claimed in U.S. Patent Application Serial No. 06/039,708, filed May 17, 1979. This battery separator composition comprises a mixture of 30 percent to 80 percent by weight of expanded perlite and 20 percent to 70 percent by weight of glass fibers, wherein the glass fibers have diameters in the range of from about 0.3 to about 1.0 micrometers and the perlite has particle sizes in the range of from about 3 to about 100 micrometers. The electrical performance properties of these compositions have been found to be eminently suitable for use in the starved electrolyte lead/acid batteries.

Continued experience with the perlite/glass fiber separator compositions and separators made therefrom have brought to light one significant problem, however. In some battery production methods, the separator is in the form of a long paper strip which is wound in a spiral fashion with the electrical plate materials to form cylindrical batteries. Typical of this type of construction are the batteries shown in the aforementioned U.S. Patent No. 3,862,861. The winding operations to form such batteries are performed at high speed and under high tensile loads. In some cases with the perlite/glass fiber paper strips, the papers have been unable to sustain that high tensile loading and have torn apart. When this occurs, of course, the winding operation must be stopped and the paper tear repaired.

It would therefore be highly desirable to have a separator material having the same electrical performance characteristics and low cost features of the papers of the prior invention, but having increased tensile strength sufficient to allow the paper to be wound rapidly into a cylindrical battery shape without significant amounts of tearing of the paper.

**Brief Summary of the Invention**

The invention herein comprises an improved composition for use as a separator in a starved electrolyte lead/acid battery which comprises a mixture of 15 percent to 75 percent by weight of expanded perlite, the perlite having particle sizes in the range of from about 30 to about 100 micrometers; 20 percent to 70 percent by weight of
glass fibers, wherein the glass fibers have diameters in the range of from about 0.3 to about 1.0 micrometers and 5 percent to 20 percent by weight of substantially acid-insoluble thermoplastic fibers. These improved compositions have been found to be essentially equivalent in all important chemical and electrical properties to the battery separator compositions of the prior invention, but to have tensile strengths some three to five times greater. The invention also includes a paper article made from this improved composition and a battery separator made from the paper.

**Detailed Description of the Invention**

The articles utilizing the compositions of this invention are denominated "separators" for the starved electrolyte lead/acid batteries, following the nomenclature of the prior patents, especially the aforesaid U.S. Patent No. 3,862,861. However, it will be recognized from the structure of these starved electrolyte batteries that the articles, unlike separators in conventional batteries, are multifunctional, in that they possess not only a separator function but also a reservoir function, wherein they serve to retain the electrolyte within the battery. It is believed that the microporous nature and the high specific surface area of the present articles, with their myriads of minute passageways and interstices, impart to the articles their ability to combine these different functions. For the purposes of this specification, therefore, the practice of the aforesaid prior patents in labeling these articles "separators" will be adhered to, but the difference between the present multifunctional articles (with their "separator/reservoir" nature) and conventional battery separators should be recognized.

The compositions herein are formed from a mixture of expanded perlite granules, small diameter glass fibers and acid-insoluble thermoplastic fibers.

Perlite is a rhyolitic glassy rock formed by volcanic action. Perlite is unique among the glassy materials in that it contains a significant proportion of combined water which, when the perlite is crushed and rapidly heated, is converted to steam and causes the perlite granules to expand or "pop" to form expanded perlite granules with volumes some 4 to 20 times greater than the volume of the original unexpanded particles. Bulk densities of the expanded
materials are commonly in the range of from about 0.03 g/cm³ to about 0.25 g/cm³. The high volume, low bulk density expanded perlite has in the past been used in a variety of applications, including as filter aids, thermal insulation, lightweight concrete aggregates and for horticultural use. However, until the invention described in the aforesaid application Serial No. 06/039,708, expanded perlite had never before been considered as having utility in electric batteries.

In the compositions of this invention the perlite will be present in the form of generally irregular particles having nominal particle sizes in the range of from about 3 to about 100 micrometers. Most suitable for use in the present invention are those grades of perlite having particle sizes in the range of from about 10 to about 35 micrometers. Suitable grades of perlite are available commercially from Johns-Manville Corporation. The perlite will be present in the composition as from about 15 percent to about 75 percent, preferably 40 percent to 60 percent, of the composition. (Unless otherwise stated, all percentages herein are by weight.)

Since perlite is a natural material, the compositions of batches taken from different ore bodies or even different parts of the same ore body will vary, sometimes widely, but normally within fairly well defined limits. Typical perlite chemical analyses show 71 percent to 75 percent SiO₂, 12 percent to 13 percent Al₂O₃, and 7 percent to 9 percent K₂O and Na₂O with the remainder being a wide variety of other oxides and elements including materials such as calcium, iron, magnesium and titanium oxides. Typical analyses are described in Industrial Minerals, page 17 (May, 1977). The exact composition of the perlite is not critical in this invention, as long as the perlite used is chemically and electrically compatible with the other materials in the present separator compositions and also in the assembled batteries.

The glass fibers used in the present compositions may be produced from any of a wide variety of glass fiber forming compositions. The fibers formed from such compositions must have average volume surface diameters in the range of from 0.3 to 1.0 micrometers. Typical glass compositions for glass fibers useful in this invention include those shown in U.S. Patent No. 3,085,887. The glass fibers will be present in the composition as from about 20
percent to about 70 percent, preferably 30 percent to 50 percent, of the composition. Compositions containing less than about 20 percent of glass fiber do not produce papers with adequate physical integrity to withstand handling, while those with more than about 70 percent glass fiber give no added electrical properties but are significantly costlier.

The third component of the improved separator compositions and articles of the present invention are acid-insoluble thermoplastic fibers in quantities of 5 to 20 percent, preferably 10 to 15 percent. Any conventional type of acid-insoluble staple or chopped thermoplastic fibers may be used. Typical among the fibers which are useful in this composition are polypropylene fibers, saran fibers (predominantly polyvinylidene chloride units in the polymer), ethylene/propylene copolymer fibers, polyethylene fiber and vinylon fibers, such as fibers of copolymers of polyvinyl chloride and polyvinyl acetate. The staple fibers or chopped fibers should have an aspect ratio (i.e., length:diameter ratio) on the order of about 1000:1. The aspect ratio may vary widely, however, as long as the staple or chopped fibers have sufficient length to provide significant increases in tensile strength to the papers and separators as compared to papers and separators of the prior invention not containing such staple or chopped fibers. Since the papers are normally wet-laid from slurries of fibers and perlite, the thermoplastic fibers should not be of undue length so that clumping and other formation problems can be avoided. Those skilled in the art of paper making will be immediately aware of the maximum and minimum practical lengths for chopped fibers or staple fibers in order to get good formation during the paper making process as described below and have good tensile strength in the finished products.

The separator articles of the present invention may also contain small amounts (up to a few percent by weight) of other materials such as unexpanded perlite, glass fragments, silica particles and the like. Because the nature of the separator is vitally important to the electrical performance of the finished battery, however, such materials should be present only if they do not detrimentally affect that electrical performance. Since the effect on electrical performance of the various types of potential impurities cannot be
readily predetermined, it is preferred that the amount of impurities be minimized and the compositions herein be composed essentially entirely of the expanded perlite, glass fibers and thermoplastic fibers. The compositions of the present invention are formed into sheets of paper, from which the separator materials of the present invention are made, in the manner of conventional paper making. The glass fibers, expanded perlite and thermoplastic fibers are dispersed in an aqueous acid slurry (pH of about 3) which is stirred so as to cause the perlite and fibers to become thoroughly and randomly mixed with each other. The perlite/fiber mixture is then deposited from the slurry onto a conventional paper making screen or wire as in a Fourdrinier machine or a Rotoformer machine to form a matted paper. For these purposes the perlite in the furnish should not contain more than about 5 percent, preferably not more than about 1 percent, of "floaters," which are perlite particles which float on the surface of the water slurry. Floaters are detrimental because they do not get incorporated into the fiber matrix of the paper, but are deposited last as the slurry drains and thus form a loose dusty layer on the surface of the paper. Quantities of floaters greater than those mentioned above merely increase the problem. The paper formed of the fibers and perlite particles is then dried and collected in a conventional manner. Following collection of the dry paper, the paper is heat treated to "seal in" the fibers. This is accomplished by heating the paper at a temperature of approximately 260°F to 280°F (125°C to 135°C) for a short period. In commercial operation, this would normally be carried on by passing the dry paper through hot press rolls where the paper would be in contact with the rolls for a few seconds. Thereafter, the paper may be cut to sizes appropriate for the various size batteries in which the separator materials are to be used.

As examples of the improved composition and papers of the present invention, two sets of materials were hand formed in sheets in the laboratory. The first sample contained 50 percent of perlite, 35 percent of glass microfibers and 15 percent of staple vinyon fibers comprising a copolymer of polyvinyl chloride and polyvinyl acetate. Fiber diameters were approximately 20 micrometers. The paper was heat
treated as described above. In the second set of experiments, an identical composition was made up with the exception that the staple fibers tested were polyethylene staple fibers produced commercially by the Crown Zellerbach Company and sold under the name "synthetic wood pulp." Estimated fiber diameter of the staple materials was in the range of 1 to 5 micrometers. Test results on samples of these two materials indicated that papers of the present invention including the thermoplastic fiber had from three to five times greater tensile strength than the perlite/glass fiber papers of the prior invention.

The papers of the present invention will not be expected to show any significant change or deterioration in electrical properties as compared to the perlite/glass fiber papers of the prior invention.

Statement of Industrial Application

The materials of the present invention find application as separators and reservoirs in starved electrolyte lead/acid storage batteries. Batteries using such materials will in turn find application for many electrical power generating uses including automotive electrical systems.
1. A composition, useful as a separator material in starved electrolyte lead/acid batteries, which comprises a mixture of 15 percent to 75 percent by weight of expanded perlite, 20 percent to 70 percent by weight of glass fibers and 5 percent to 20 percent by weight of acid-insoluble thermoplastic fibers, said glass fibers having diameters in the range of from about 0.3 to about 1.0 micrometers and said perlite having particle sizes in the range of from about 3 to about 100 micrometers.

2. A composition as in Claim 1 consisting essentially of said expanded perlite, glass fibers and thermoplastic fibers.

3. A composition as in Claims 1 or 2 wherein said expanded perlite is present as from 40 percent to 60 percent by weight of the composition, said glass fibers are present as from 30 percent to 50 percent by weight of the composition, and said thermoplastic fibers are present as on the order of about 10 to 15 percent by weight.

4. A composition as in Claims 1 or 2 wherein said expanded perlite has particle sizes in the range of from about 10 to about 35 micrometers.

5. A composition as in Claims 1 or 2 wherein said thermoplastic fibers are selected from the group consisting of saran fibers, polypropylene fibers, ethylene/propylene copolymer fibers, vinyon fibers and polyethylene fibers.

6. A composition as in Claim 5 wherein said thermoplastic fibers are in the form of staple fibers.

7. A paper useful as a separator material in a starved electrolyte lead/acid battery comprising the composition of Claim 1 in matted form.

8. A paper useful as separator material in a starved electrolyte lead/acid battery comprising the composition of Claim 2 in matted form.

9. A paper useful as separator material in a starved electrolyte lead/acid battery comprising the composition of Claim 5 in matted form.

10. A paper useful as separator material in a starved electrolyte lead/acid battery comprising the composition of Claim 6 in matted form.
11. A battery separator for a starved electrolyte lead/acid battery formed from a paper as in Claim 7.

12. A battery separator for a starved electrolyte lead/acid battery formed from a paper as in Claim 8.

13. A battery separator for a starved electrolyte lead/acid battery formed from a paper as in Claim 9.

14. A battery separator for a starved electrolyte lead/acid battery formed from a paper as in Claim 10.
**INTERNATIONAL SEARCH REPORT**

**International Application No.** PCT/US 81/00157

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### I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

**INT. CL.** 3 H01M 2/16  
**US. CL.** 429/247, 106/52, 252/378P

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

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### III. DOCUMENTS CONSIDERED TO BE RELEVANT

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* Special categories of cited documents:

- **"A"** document defining the general state of the art
- **"E"** earlier document but published on or after the international filing date
- **"L"** document cited for special reason other than those referred to in the other categories
- **"O"** document referring to an oral disclosure, use, exhibition or other means
- **"P"** document published prior to the international filing date but on or after the priority date claimed
- **"T"** later document published on or 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

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### IV. CERTIFICATION

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**International Searching Authority**

ISA/US

**Signature of Authorized Officer**

Anthony N. Kapas

Form PCT/ISA/210 (second sheet) (October 1977)
V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers __________, because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers __________, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (supplemental sheet (2)) (October 1977)