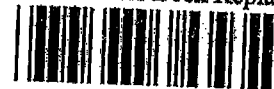


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**Patent claims**

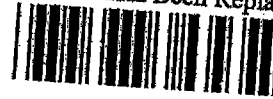
1. Negative electrode for gastight alkaline storage
5 batteries, which has a carbon black-containing gas-
consumption layer, characterized in that the carbon black
component is produced by mixing an aqueous carbon black
dispersion with an aqueous PTFE dispersion, a surfactant
used as emulsifier in both dispersions being uniformly
10 either of cationic, anionic or nonionic type.
2. Negative electrode according to Claim 1, charac-
terized in that the carbon black component contains
polyacrylic acid esters as thickening agent in order to
adjust the viscosity.
- 15 3. Negative electrode according to Claim 1 or 2,
characterized in that the carbon black content of the
first mixture component is 1 to 20% and the PTFE content
of the second mixture component is 1 to 60%.
4. Negative electrode according to Claim 3, charac-
20 terized in that the carbon black content of the first
mixture component is 0.5 to 5% and the PTFE component of
the second mixture component is 2 to 20%.
5. Negative electrode according to one of Claims 1
to 4, characterized in that the primary particle size of
25 the carbon black used is 0.001 to 0.01 μm , at a BET
surface area of 200 to 2000 m^2/g , and the primary particle
size of the PTFE used is 0.01 to 0.5 μm .
6. Negative electrode according to Claim 5, charac-
terized in that the primary particle size of the carbon
30 black is 0.01 to 0.07 μm and the primary particle size of
the PTFE is 0.05 to 0.2 μm .
7. Process for producing a negative electrode
according to one or more of Claims 1 to 6, characterized
in that the mixture comprising a carbon black dispersion
and a PTFE dispersion, and optionally a thickening agent,
35 is applied to the electrode surface.
8. Process according to Claim 7, characterized in

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that the mixture is applied by immersion or spraying.

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Negative electrode for gastight alkaline storage
batteries which has a carbon black-containing gas-
consumption layer

5 The invention relates to a negative electrode for
gastight alkaline storage batteries which has a carbon
black-containing gas-consumption layer.

10 In order to be able to charge gastight storage
batteries of this system with as high currents as pos-
sible, their negative electrodes are often provided, in
order to accelerate the oxygen consumption, with
auxiliary electrodes which are made of a catalytically
active material and which are at the same potential as
the negative main electrode.

15 According to German Offenlegungsschrift 35 34
758, such an electrode arrangement in an Ni/Cd button
cell, for example comprising the negative electrode in
tablet form pressed into a nickel-wire gauze basket and
a carbon-containing mixture of active carbon, conductive
carbon black and PTFE as binder, which mixture is rolled
20 into the nickel-wire gauze material of the basket lid. It
is also known from German Offenlegungsschrift 34 33 544
to coat a negative cadmium electrode directly with a
catalytically active carbon material in dry form. Before
the dry application of the carbon material, for example
25 by dusting, the electrode is moistened with a dispersion
of a water-soluble cellulose ether (tradename: Tylose).
Cellulose ethers of this kind, such as methylcellulose or
carboxymethylcellulose, which generally find application
as thickeners, binders and suspending agents, act in this
30 case mainly as adhesives.

In a dry coating, however, disadvantages may
arise as a result of the fact that, on the one hand, only
the outer electrode surface and not the inner pores are
coated and, on the other hand, irregularities are present
35 in the coating thickness which have the result that the
electrolyte absorption of the negative electrode is
impaired; as a result, long exposure times of the cell
are necessary during the production.



Wet coatings based on aqueous dispersions have again given little satisfaction because, in the course of the cyclic charge/discharge operation, the coating loses some of its hydrophobic nature. This results in a deterioration of the gas-consumption kinetics, which are unalterably associated with the maintenance of three-phase boundary layers composed of electrically conducting solid-state surface, gas phase and the liquid electrolyte. As a consequence, a high cell internal pressure is established which contributes to the shortening of the service life of the cell. A further disadvantage of aqueous dispersions hitherto used is that they have a tendency to demix and separate the carbon component and the PTFE component.

The object of the invention is therefore to provide a negative electrode for, in particular, gastight NiCd and NiH cells, which electrode is surface-coated with carbon black for the purpose of catalytic oxygen recombination, the material for the carbon black application being intended to be readily and uniformly absorbed on the negative electrode and to have a long active life under the conditions of battery operation.

According to the invention the object is achieved with an electrode such as is defined in Claim 1.

According to Claim 1, the carbon black content of the layer is formed from a dispersion which is the mixing product of two aqueous dispersions of which one has a carbon black content of 1 to 20%, preferably 0.5 to 5%, for example approximately 2%, in addition to an added emulsifier composed of a cationic, anionic or nonionic surfactant and the other is a PTFE dispersion containing 1 to 60% PTFE, preferably 2 to 20%, for example approximately 10%, and also contains an emulsifier. According to the invention, the emulsifiers in the two mixture components are of the same type in regard to their ionic activity, i.e. both are either only cationic or only anionic or nonionic. The carbon black used in the first mixture component has, according to the invention, a BET surface area of 200-2000m²/g, with a primary particle



size of 0.001 to 0.1 μm , preferably 0.01 to 0.07 μm , for example approximately 0.05 μm . A highly suitable carbon black product is, for example, obtainable under the tradename Akzo Ketjenblack ED 310.

5 The PTFE used for the second mixture component should, on the other hand, have a primary particle size of 0.01 to 0.5 μm , preferably 0.05 to 0.2 μm , for example approximately 0.1 μm . Suitable products have the name Hoechst PTFE 5032 or DuPont Teflon N30.

10 No flocculation or coagulation must occur during the mixing of these two dispersions. According to the invention, this is achieved by stabilizing both the carbon black dispersion and the PTFE dispersion with a surfactant of the same ionic type. In addition, a
15 buffering of the two dispersions at the same pH markedly increases the long-term stability of the final mixture. For the purpose of uniform application of the carbon black dispersion according to the invention to the negative electrode, it is advantageous to establish a certain
20 dispersion viscosity. In the case of known gas-consumption dispersions, the methylcelluloses mentioned above are generally used for this purpose. With their beneficial properties, as hydrophilic colloids, of making the aqueous dispersions more stable and, in particular,
25 of acting as a protective colloid with respect to the PTFE, these additives contribute, however, to a loss of hydrophobicity of the electrode.

 It was found that this deficiency can be eliminated by other polymers which have a thickening action
30 and which do not behave as protective colloids. According to the invention, the addition of polyacrylic acid esters, for example a product having the tradename Akzo Carbopol 941, is very advantageous for adjusting the dispersion viscosity.

35 In contrast to dry mixtures, the mixing of the dispersions described, including thickeners, can be achieved very simply by any desired stirring tool and also by tumbling or rotating the mixing vessel. High gravitational forces and long mixing times are not



necessary. The dispersion produced is notable for outstanding long-term stability and neither coagulation nor demixing occur. This provides a substantial process simplification in the coating of the electrode.

5 The stability of the dispersion according to the invention is closely related to the size and structure of its particles:

during mixing, the carbon black particles, which are mostly present in aggregates having diameters of between
10 0.02 and 0.2 μm , are absorbed on the surface of the discrete spherical PTFE particles and, in doing so, disintegrate into numerous small primary particles or filaments, whose size varies between 0.001 and 0.1 μm . They "spread", so to speak, around the PTFE particle and
15 envelope it like a spherical shell. The latter is not, however, continuous but is perforated by a multiplicity of fissures and, consequently, is highly porous. It remains firmly bound to the PTFE surface so that a double layer is produced which is composed of hydrophobic PTFE
20 and outer carbon having a high catalytic surface area.

In addition to these spherical particles, berry-shaped particles are also typical of the dispersion according to the invention. They are produced by agglomeration of a few PTFE particles with an equal number of
25 carbon particles which are about the same size but are, however, agglomerates of primary particles.

The two particle shapes of the dispersion according to the invention are illustrated with reference to two figures.

30 Figure 1 shows a spherical PTFE/C particle.

Figure 2 shows a berry-shaped PTFE/C particle.

According to Figure 1, the discrete PTFE particle 1 is surrounded by a multiplicity of smaller C primary particles 2 which have been produced by the disintegration of larger aggregates during the mixing. The
35 diameter of the PTFE particle is, for example, 0.1 μm and the diameter of the C primary particle is 0.05 μm , resulting in a total diameter of the PTFE/C particle of 0.2-0.3 μm , depending on the concentration of C particles



in the spherical envelope.

Even as the admixture of carbon increases, the spherical layer continues to be penetrated by sufficient pores and fissures 3 for an access of oxygen to the carbon particle always to remain ensured under the hydrophobizing influence of the PTFE core.

Since the PTFE core and the carbon envelope furthermore enclose a surfactant layer 4 between them and the carbon envelope also has an outer surfactant layer, a type of sandwich structure is characteristic of the "primary particle" of the dispersion according to the invention. As has been demonstrated by scanning electron microscopy, the morphology of these sandwich micro-aggregates may vary from irregular shapes to spherical particles (shown here in idealised form).

The berry-type shape, also to be observed under the scanning electron microscope, of a "primary particle" according to the invention shown in Figure 2 generally comprises 2 to 3 PTFE particles and an equal number of carbon particles, including their surfactant coatings. The size of these particles generally does not substantially exceed that of the "primary particle" in Figure 1.

The advantages of the gas-consumption dispersion according to the invention may be summarized as follows: The dispersion is found to be very stable. The discrete individual particles do not exhibit any tendency to agglomeration. They make possible either a subsequent coating of a finished electrode strip (for example, produced by the electrodeposit method according to German Patent Specification 28 22 821) or else a homogeneous addition to the active-mass paste for pasting individual electrodes. The dispersion reaches not only the outer geometrical electrode surface, but also, as a result of the small size of the sandwich particles, the inner pores of the electrode, with the result that the coated, catalytically active surface area is markedly increased.

Suitable coating processes are immersion jet coating, or spraying freely and very uniformly adjustable, reproducible layer thickness being capable of being



achieved in every case.

Owing to the microdispersity of the system and the intimate contact of carbon and PTFE support, the electrode coated with the dispersion according to the invention is notable for the durability of its hydrophobic nature and, consequently also for gas-consumption kinetics having long-term stability.

The gas-consumption properties can be markedly improved by replacing the standard methylcellulose thickeners with other viscosity-increasing polymers which do not, however, act as protective colloids.

In contrast to a dry coating, the electrolyte absorption of a cell is markedly improved by the wet coating of the negative electrode with the dispersion according to the invention, with the result that shorter processing times are possible in the addition of electrolyte and, consequently a faster and more efficient cell production is possible. A cell having an electrode coated in this way exhibits a marked improvement in the fast charging capability and the overcharging capability, even after large numbers of cycles; this also manifests itself in a markedly increased service life.

The same cell also exhibits, even after a large number of cycles, a virtually unaltered charging characteristic, with the result that a switching off during overcharging by means of a voltage difference signal is possible even after a long operating life.