Title: HIGH SOLIDS CONTENT BOEHMITE ALUMINA DISPERSIONS AND COATED SUBSTRATES MADE THEREFROM

Abstract: A composition comprising an aqueous dispersion containing from 25 to 40% by wt. of a solid particulate boehmite alumina which has a surface area of from 100 to 160 m²/g and a crystallite size (120 plane) of from 140 to 350 Angstroms, the dispersion having a pH in the range of 3-5.
HIGH SOLIDS CONTENT BOEHMITE ALUMINA DISPERSIONS
AND COATED SUBSTRATES MADE THEREFROM

BACKGROUND OF THE INVENTION

5 FIELD OF THE INVENTION

The present invention relates to aqueous dispersions of boehmite alumina
and, more particularly, to such dispersions containing a high solids content of
boehmite alumina. The present invention also relates to coated substrates, e.g.,
recording sheets and the like, made from the boehmite alumina dispersions.

10 DESCRIPTION OF PRIOR ART

Aqueous dispersions of alumina, particularly boehmite alumina, are well
known and have wide utility in many industrial applications. In particular, such
dispersions are used as coatings on substrates of various types. One, non-
limiting example, of a coated substrate which is made from aqueous dispersions
of boehmite alumina is a recording sheet used with ink jet printers.

Regardless of the end use, the desired property of an aqueous alumina
dispersion is to have as high a solids content as possible but with low viscosity
and no other deleterious rheological properties. Furthermore over time, the
dispersion should be stable (non-settling) and not become viscous.

Aqueous dispersions or sols of boehmite aluminas in concentrations up to
25% by wt. based on Al₂O₃ content (30-32% total solids content), are known.
Generally speaking, about 30-32% by wt. total solids boehmite alumina is
considered the maximum stable concentration of alumina dispersion that can be
made and stored with reasonable assurance that the sol will remain stable over
time and not develop undesirable rheological properties. If it is desired to make
dispersions/sols with only short shelf life or where the risk of gelling is of no
consequence, higher concentration dispersions can be made.

Clearly it would be desirable in many applications to have an aqueous
alumina sol which had a solids content as high as possible, a stable shelf life,
low viscosity, and in which the rheological properties did not degrade over time.
SUMMARY OF THE INVENTION

In a preferred aspect, the present invention provides a composition comprising an aqueous dispersion containing from 25 to 40% by wt. total solids of a particulate boehmite alumina, having a surface area of from 100 to 160 m²/g, and a crystallite size (120 plane) of from 140 to 350 Ang., the dispersion having a pH in the range of from 3-5.

In another preferred aspect, the present invention provides a process for producing coated substrates comprising providing a suitable substrate, applying an aqueous boehmite alumina substrate as described above to the substrate to produce a wet coated substrate and drying the wet coated substrate.

Another preferred feature of the present invention involves a recording sheet which comprises a substrate having a surface and a layer of an adsorbent on the surface of the substrate, the adsorbent being capable of receiving an image forming medium, e.g., ink, to form an image, the adsorbent layer comprising a particulate boehmite alumina having a surface area of from 100 to 160 m²/g and a crystallite size of from 140 to 350 Ang.
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the effect of surface area on viscosity for dispersions of various solids loading.

Figure 2 is a graph showing the effect of pH on viscosity for dispersions of various solids loading.

Figure 3 is a graph showing the long-term stability of concentrated dispersions of aluminas of varying surface area.

Figure 4 is a graph showing dispersion viscosity as a function of alumina crystallite size.
DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

Boehmite alumina has the following general formula:

$$Al_2O_3 \cdot n(OH)_{2n} \cdot mH_2O$$

wherein n is an integer from 0 to 3 and m is a value within the range of from 0 to 10, preferably from 0 to 5, provided that m and n are not zero at the same time. The water grouping, mH_2O indicates water of hydration (free water) which for the most part is not involved in the crystal lattice and accordingly can assume a non-integral value. As is well known to those skilled in the art, boehmite aluminas can be essentially a total boehmite structure or a pseudoboehmite structure containing excess water between (020) planes. In an X-ray diffraction pattern, the pseudoboehmite structure shows a broader diffraction peak than a complete boehmite structure. As a complete boehmite structure and the pseudoboehmite structure cannot be clearly distinguished, a boehmite alumina according to the present invention includes both boehmite structures unless specified otherwise.

Numerous methods for producing boehmite aluminas or hydrated aluminas used in the present invention can be employed. For example, the aluminum hydrate can be produced by the Bayer process. A preferred method of preparing the alumina hydrates of the present invention is disclosed in U.S. Patent 4,676,928, incorporated herein by reference for all purposes. As noted in that patent, aluminas which are useful in the present invention can be obtained by the hydrolysis of aluminum alkoxides which are produced by reacting a low molecular weight alcohol, particularly a branched chain alcohol, with an aluminum bearing material. Such aluminum bearing materials include pure
aluminum as well as aluminum alloys and mixed alloy scrap. Typical methods for preparing such aluminum alkoxides are shown, for example, in U.S. Patent 4,242,271, incorporated herein by reference for all purposes. The aluminum alkoxide can be hydrolyzed, in a well known manner, such as by the process taught in U.S. Patent 4,202,870, incorporated herein by reference for all purposes. Especially preferred are aluminas obtained from the hydrolysis of aluminum alkoxides derived from Ziegler chemistry.

The boehmite aluminas of the present invention obtained by methods described above can be subjected to crystallite growth by a hydrothermal treatments such as set forth in U.S. Patents 4,676,928 and 5,055,019, incorporated herein by reference for all purposes. In general, in the present invention, hydrothermal treatment or other crystal growth techniques are employed until aluminas having the desired physical characteristics for use in the present invention are achieved.

In part, the present invention is based upon the surprising finding that if the surface area of the particulate boehmite alumina is between 100 and 160 m²/g, the crystallite size between 140 to 350 Ang., and the pH of the aluminum dispersion or sol is in the range of 3 to 5 preferably 3 to 4, dispersions of up to 40% by wt., especially 32 to 40% by wt., solids can be made that are reasonably fluid and stable over time. In particular, dispersions containing 25 to 35% by wt. solids can be made that are virtually water thin and have long-term stability. Additionally, these dispersions exhibit Newtonian viscosity behavior. The
dispersions of the present invention require no stabilizers other than the acid used in the hydrothermal treatment process.

As noted, the boehmite aluminas of the present invention will have a crystallite size (120 x-ray plane) of from 140 to 350 Ang., preferably 200 to 300 Ang.

It has also been found preferable that the boehmite alumina have a porosity of less than 1 ml/g and more preferably from about 0.4 to about 0.8 ml/g. It has been found that if the porosity of the alumina is too high, water absorption is increased so that the effective solids are increased in the dispersion with a concomitant increase in viscosity.

As noted above, the aluminas of the present invention can be prepared by a variety of crystal growth processes, a particularly preferred method being the hydrothermal treatment disclosed in U.S. Patent 4,676,928.

To more fully illustrate the invention, the following non-limiting examples are presented. In the following examples, the aluminas used where boehmite aluminas produced pursuant to the method disclosed in U.S. Patent 4,676,928, i.e., by the hydrolysis of aluminum alkoxides. The aluminas used are marketed under the trademark DISPAL® by Sasol North America, Inc.

In the examples which follow, the percent solids in the dispersions are calculated as boehmite alumina less free water, i.e., water that can be removed at about 120°C. Typically, boehmite aluminas contain from about 3 to about 6% by wt. free water depending on the crystallite size.
The table below shows the relationship between the solids content for various dispersions versus parameters such as pH, crystallite size, surface area and viscosity. Also shown is a procedure for measuring viscosity.

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<tr>
<th>Test</th>
<th>Dispersion pH</th>
<th>Crystallite Size 120 Angstroms</th>
<th>Surface Area m²/g</th>
<th>Viscosity 25% Solids</th>
<th>Viscosity 30% Solids</th>
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Procedure:
1. Blend 300 total batch size for 5 minutes in a 400 ml beaker.
2. Record viscosity at 3 minutes after starting spindle.

Note: Brookfield Viscometer Viscosities measured with #4 Spindle @ 20 rpm 10,000 value = over range for viscometer @ 10,000 centipoise
* PH adjusted after powder dispersed
** New Sample

Based on the data in the table, several graphs were prepared showing various relationships between solids loadings and parameters such as viscosity, pH, crystallite size and surface area. Turning first to Figure 1, the effect of surface area on dispersion viscosity is shown. As can be seen at low solids concentrations, the dispersions are fluid over a wide range of surface areas.

However, as solids loadings increase, the window of low viscosity becomes narrower. Note in particular that when the aluminas have surface areas below about 100 m²/g, there is an increase in viscosity. As can also be seen when the surface area is between about 100 and 160 m²/g, acceptable viscosities are achieved even at solids loadings of 40% by wt.
Turning to Figure 2, which shows the effect of pH on viscosity, it can be seen that the lowest viscosity is achieved when the pH of the dispersions is between about 3 and 4.

Figure 3 shows the long-term stability of various dispersions. As can be seen, with the surface areas of the aluminas within the range of 100 to 160 m²/g, and crystallite sizes within the range of 140 to 350 Angstroms, all samples were stable for at least 38 days, where stable is defined as no substantial settling of the alumina from the sol.

Lastly, Figure 4, shows the effect of crystallite size on dispersion viscosity. As can be seen from Figure 4, within a crystallite size (120 plane) range of from about 140 to 350 Angstroms, all of the dispersions had an acceptable viscosity. Note in particular that at small crystallite sizes, i.e., below about 140 Angstroms, viscosity increases dramatically.

As can be seen from the above data, stable dispersions of boehmite alumina which have acceptable viscosity can be achieved if the alumina dispersions have a pH of from about 3 to about 5, the crystallite size of the alumina (120 plane) is from about 140 to 350 Angstroms and the surface area is from about 100 to 160 m²/g.

The boehmite dispersions of the present invention as described above, can be used in a wide variety of applications. Indeed, the alumina dispersions of the present invention are applicable to any use wherein it is desired to have a high solids content dispersion which has low viscosity and is therefore readily pumpable, spreadable or even sprayable. For example, in the process of
making coated papers, films and other recording media, there is often a need to apply a high level of alumina solids to the substrate. Although this can be accomplished, with prior art dispersions, by applying repeated coats of a low solids dispersion to the substrate, obviously it is more desirable and far more economical if the desired thickness can be achieved with a single coating. Obviously this can only be accomplished if the dispersion contains a high enough loading of solids. Thus, while the desired thickness can be accomplished by multiple layer applications of the dispersions, costs increase because of the need for multiple coating and drying steps. As to using a dispersion which contains a high solids loading content, with prior art compositions, the viscosity becomes a problem due to the high solids loading. In this regard, at high solids loadings prior art dispersions can be very thick and have poor viscosity behavior such as shear thickening. Moreover there is a tendency of the bulk dispersion to become viscous and non-fluid with time. When this occurs, the alumina dispersion cannot be evenly coated on the substrate and in fact cannot even be stored for later use.

Thus, in one application of the dispersions of the present invention, the dispersion can be applied to a suitable substrate, e.g., paper, film or the like, to produce a wet or coated substrate and the coated substrate dry to produce a recording sheet onto which an image forming medium can be applied. Basically, by using the dispersions of the present invention, there can be formed a recording sheet comprising a substrate, e.g., paper, which has a surface, the surface having a layer of absorbent formed from the alumina dispersion. The
absorbent is capable of receiving an image forming medium such as ink, pigment, paint or the like, and will comprise a particulate boehmite alumina having a surface area of from 100 to 160 m²/g and a crystallite size (120 plane) of from 140 to 350 Angstroms.

When producing a recording sheet or the like from the alumina dispersions of the present invention, it will be understood by those skilled in the art that the layer of absorbent forming part of the recording sheet, will include other ingredients commonly used on recording media to obtain various desired properties. Thus, for example, additives including various metal oxides, sols of divalent or polyvalent metals and cationic organic substances can be employed as the metal oxide, oxides or hydroxides such as silica, boria, silica boria, silica magnesia, titania, zirconia and zinc oxide. As examples of the sols of di- or polyvalent metals, non-limiting examples include calcium carbonate and barium sulphate as well as calcium nitrate or halides such as magnesium chloride, calcium bromide, calcium iodine, etc. As the cationic organic substance, non-limiting examples include quaternary ammonium salts, polyamines and alkyl amines.

In addition to the above additives, and in forming a recording sheet using the alumina dispersions of the present invention, binders can also be employed, non-limiting examples of such binders including water soluble polymers such as polyvinyl alcohol and modified products thereof, starch and modified products thereof, gelatin and modified products thereof, casein and modified products thereof, gum arabic, etc.
It is also known that organic acids can be employed in preparing the recording media or sheets of the present invention. Numerous, non-limiting examples of such organic acids are disclosed in U.S. Patent 6,565,950, incorporated herein by reference for all purposes.

When the alumina for dispersions of the present invention are used in forming recording media, there can also be incorporated viscosifiers, pH adjusting agents, lubricants, fluidity modifiers, surfactants, defoaming agents, water poufing agents, anti-foamers, releasing agents, etc.

Modifications of the compositions, procedures and conditions disclosed herein that will still embody the concept of the improvements described should readily suggest themselves to those skilled in the art, and are intended to be encompassed within the spirit of the invention presently disclosed herein as well as the scope of the appended claims.
WHAT IS CLAIMED IS:

1. A composition comprising an aqueous dispersion containing from 25 to 40% by wt. of a solid, particulate, boehmite alumina having a surface area of from 100 to 160 m²/g, and a crystallite size (120 plane) of from 140 to 350 Ang., the dispersion having a pH in the range of 3-5.

2. The composition of Claim 1, wherein the pH is in the range of 3-4.

3. The composition of Claim 1, wherein the dispersions contain from 32 to 40% by wt. boehmite alumina.

4. The composition of Claim 1, wherein the dispersion contains from 25-35% by wt. boehmite alumina.

5. The composition of Claim 1, wherein the boehmite alumina is produced by hydrolysis of an aluminum alkoxide.

6. The composition of Claim 1, where in the boehmite alumina is subjected to hydrothermal treatment.

7. A process for producing coated substrates comprising:
   providing a substrate having a surface;
applying an aqueous dispersion to said surface of said substrate, said aqueous dispersion containing from 25 to 40% by wt. of a solid particulate, boehmite alumina, having a surface area of from 100 to 160 m²/g, and a crystallite size (120 plane) of from 140 to 350 Ang., the dispersion having a pH of from 3-5, to produce a wet coated substrate; and
drying the wet coated substrate.

8. The process of Claim 7, wherein the pH is in the range of 3-4.

9. The process of Claim 7, wherein the dispersions contained from 32 to 40% by wt. boehmite alumina.

10. The process of Claim 7, wherein the dispersion contains from 25-35% by wt. boehmite alumina.

11. The process of Claim 7, wherein the boehmite alumina is produced by hydrolysis of an aluminum alkoxide.

12. The process of Claim 7, where in the boehmite alumina is subjected to hydrothermal treatment.

13. A recording sheet comprising:
a substrate having a surface; and
a layer of adsorbent on said surface of said substrate, said adsorbent being capable of receiving an image forming medium to form an image, said adsorbent layer comprising a solid particulate, boehmte alumina having a surface area of from 100 to 160 m$^2$/g and a crystallite size (120 plane) of from 140 to 350 Ang.
Figure 1: Effect of Surface Area on Dispersion Viscosity

- 25% Solids
- 30% Solids
- 35% Solids
- 40% Solids

Dispersion Viscosity, cp

Powder Surface Area, m²/g
Figure 2. Effect of pH on the Viscosity
Figure 4. Boehmite Dispersion Viscosity as a Function of Crystallite Size

- 25% Solids
- 30% Solids
- 35% Solids
- 40% Solids

Crystallite Size, 120 Plane, Ang.

Dispersion Viscosity, cp