

COMPOUND BASED ON YTTRIUM OR HOLMIUM WHICH IS  
REDISPERSIBLE IN THE FORM OF A SOL

The present invention relates to a compound based on yttrium or holmium which is redispersible in the form of a  
5 sol.

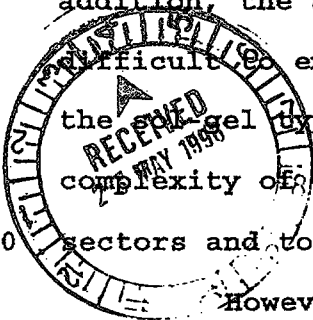
Sols or colloidal dispersions are particularly advantageous for the production of thin coatings on substrates, for example in the fields of electronics and optics.

10 These coatings allow the substrate to be endowed with specific properties, for example of nonreflection, of transparency, of a filter or for protection. These properties are provided by the presence of inorganic particles whose size is generally smaller than 0.1  $\mu\text{m}$ .

15 While sols offer such particle sizes, they have, in addition, the advantage of being much less costly and difficult to employ than coatings provided by techniques of the sol-gel type or vacuum evaporation. The cost and complexity of these limits their use to high-technology  
20 sectors and to substrates or systems of suitable geometry.

However, the use of sols is limited by some instability over time, resulting in sedimentation. In addition, the cost of transport is always increased by the fact that, besides the active component, the liquid phase in  
25 which the latter is suspended must be conveyed.

It is consequently particularly advantageous to have



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a solid product capable of being dispersed or redispersed to give a colloidal suspension. The present invention seeks to provide such a product.

5 The present invention provides a compound in solid form, based on an yttrium or holmium hydroxide and on an anion of a monovalent acid which has a pKa of from 2.5 to 5.0, which compound is dispersible or redispersible in water in a proportion of at least 80% and predominantly in the form of a colloidal dispersion.

10 The present invention also provides a process for the preparation of such a compound which comprises spray-drying a colloidal dispersion based on an yttrium or holmium hydroxide and on an anion of a monovalent acid which has a pKa of from 2.5 to 5.0.

15 The present invention further provides a colloidal dispersion obtained by suspending or resuspending the abovementioned compound.

The present invention additionally provides the use of such a dispersion for the production of a coating on a  
20 substrate.

The compound of the invention is based on yttrium or holmium in the form of a hydroxide, it being possible for the term "hydroxide" to apply here also to products in the oxyhydroxide form.

25 The hydroxide is present in the compound with an anion of an acid.

This is a monovalent acid whose pKa is from 2.5 to 5.0.

This acid is preferably soluble in water.

Examples of such an acid are acetic acid, formic acid, propionic acid and chloroacetic acid.

The compound of the invention is in the form of a generally pulverulent solid. Its particle size (mean particle  
5 size measured by scanning electron microscopy (SEM)) may be not more than 10  $\mu\text{m}$ . It may be more particularly not more than 5  $\mu\text{m}$  and at least 1  $\mu\text{m}$ .

In addition, the compound of the invention exhibits two specific characteristics:

10 On the one hand, it is dispersible or redispersible in water. On the other hand, it disperses or redisperses predominantly in the form of a colloidal dispersion or sol.

The dispersibility is defined as  $(P_1 - P_2)/P_1$ , expressed as a percentage,  $P_1$  being the initial mass of  
15 product suspended in water and  $P_2$  being the mass of dry residual precipitate obtained after centrifuging the suspension, separating the mother liquors and the precipitate and drying the latter. The water suspension is preferably at neutral, or optionally slightly acidic pH (e.g. a pH of 4).

20 This dispersibility is measured by placing 1 g of product in a calibrated 50-ml flask; this is made up with water to 50 ml and shaken for 15 minutes. The suspension obtained is centrifuged at 4500 rev/min for 10 min. The mother liquors are then separated from the precipitate, which  
25 is dried overnight at 120°C.

The dispersibility of the compound of the invention is thus at least 80%. It may be at least 90% and may be situated from 95 to 100%.

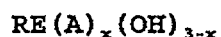
Furthermore, the compound of the invention disperses

or redisperses predominantly in the form of a colloidal dispersion. In other words, this means that, once dispersed or redispersed in water, most of the compound is in the form of a sol and not of a solution.

5                This property is measured by subjecting the aqueous medium obtained by dispersing or redispersing the compound in water to ultracentrifuging and by measuring the mass of precipitate obtained after this ultracentrifuging. This mass corresponds to the portion of the species present in the  
10 dispersion in colloidal form; the other portion in the form of solution is in the mother liquors. The mass of precipitate corresponds to at least 60%, more particularly at least 75%, of the mass of compound initially introduced into the dispersion.

15                In the present case the compound is dispersed in water and is centrifuged at 4500 rev/min for 10 minutes. The aqueous supernatant obtained is next subjected to centrifuging at 50,000 rev/min for 12 hours.

                 According to one embodiment of the invention, the  
20 compounds of the invention may have the formula:



in which:

RE denotes yttrium or holmium;

A denotes the anion of the abovementioned monovalent  
25 acid; and

x is smaller than 2.5 and greater than 1.

x may be more particularly from 1.1 to 2.2 and still more particularly from 1.2 to 1.8.

A process for the preparation of the compound of the

invention will now be described.

This process consists essentially in starting from a colloidal dispersion based on an yttrium or holmium hydroxide and on an anion of a monovalent acid which has a pKa of from  
5 2.5 to 5.0 and in spray-drying this dispersion.

The starting colloidal dispersion may be obtained by reacting an yttrium or holmium oxide with the acid of the type described above and heating the reaction mixture obtained.

10 Reference may be made to FR-A-2,620,437 in the name of the Applicant Company, the teaching of which is incorporated here in the present application, which describes the preparation of such a dispersion.

According to a preferred embodiment of the  
15 invention, the starting oxide used for the preparation of the dispersion is an oxide with a purity of at least 99% and more particularly of at least 99.99%.

The quantity of acid employed for this specific preparation of the starting dispersion is deficient in  
20 relation to stoichiometry; the molar ratio of the acid used to the rare-earth oxides, expressed as metal cation, is less than 2.5:1 and higher than 1:1.

The heating temperature is generally from 50°C to the reflux temperature of the reaction mixture. This  
25 temperature is preferably from 70 to 100°C.

The heating period can vary and is proportionately shorter the higher the temperature. Once the reaction temperature is reached, it is generally maintained for 1 to 4 hours.

The process of the invention is characterized in that colloidal dispersion is spray-dried.

Spray-drying is drying by spraying the mixture into a hot atmosphere. The spraying may be carried out by means of any sprayer known per se, for example using a spraying nozzle of the watering-can or other type. So-called turbine sprayers can also be employed. With regard to the various spraying techniques capable of being used in the present process, reference may be made especially to the fundamental work by Masters, entitled "Spray-Drying" (second edition, 1976, George Godwin publishers - London).

In the case of spraying employing equipment of the type described above, the work will generally be carried out with a solid exit temperature of from 90 to 130°C.

It will be noted that the spray-drying operation can also be carried out by means of a "flash" reactor, for example of the type developed by the Applicant Company and described particularly in FR-A-2,257,326, FR-A-2,419,754 and FR-A-2,431,321. In this case the processing gases (hot gases) are driven in a helical motion and flow into a vortex well. The mixture to be dried is injected along a trajectory coinciding with the axis of symmetry of the helical trajectories of the said gases, and this allows the momentum of the gases to be transferred completely to the mixture to be processed. The gases thus in fact fulfil a dual function: on the one hand the pulverization, that is to say the conversion of the initial mixture into fine droplets and, on the other hand, the drying of the droplets obtained. Furthermore, the extremely short residence time (generally

shorter than approximately 1/10 second) of the particles in the reactor has the advantage, among others, of limiting possible risks of superheating as a result of excessively long contact with the hot gases.

5                Depending on the respective flow rates of the gases and of the mixture to be dried, the entry temperature of the gases is generally from 400 to 900°C and more particularly from 600 to 800°C, and the temperature of the dried solid is generally from 110 to 150°C.

10              As far as the flash reactor referred to above is concerned, reference may be made especially to Figure 1 of FR-A-2,431,321.

                This consists of a combustion chamber and of a contact chamber made up of a double cone or of a truncated  
15 cone whose upper part diverges. The combustion chamber opens into the contact chamber via a narrow passage.

                The upper part of the combustion chamber is provided with an opening allowing the fuel phase to be introduced.

                Furthermore, the combustion chamber includes a  
20 coaxial inner cylinder, thus defining inside it a central zone and an annular peripheral zone, having perforations situated, for the most part, towards the upper part of the apparatus. The chamber includes at least six perforations distributed over at least one circle, but preferably over a  
25 number of axially spaced circles. The total area of the perforations situated in the lower part of the chamber may be very small, for example of the order of 1/10 to 1/100 of the total area of the perforations of the said coaxial inner cylinder.

The perforations are usually circular and are of very small thickness. The ratio of their diameter to the wall thickness is preferably at least 5:1, the minimum wall thickness being limited only by mechanical requirements.

5           Finally, a bent pipe opens into the narrow passage, the end of which opens onto the axis of the central zone.

The gaseous phase driven in a helical motion (and consequently called the helical phase) is made up of a gas, generally air, introduced into an orifice made in the annular  
10 zone; this orifice is preferably situated in the lower part of said zone.

In order to obtain a helical phase at the narrow passage, the gaseous phase is preferably introduced at a low pressure into the abovementioned orifice, that is to say at a  
15 pressure lower than 1 bar and more particularly at a pressure of from 0.2 to 0.5 bar above the existing pressure in the contact chamber. The speed of this helical phase is generally from 10 to 100 m/s and preferably from 30 to 60 m/s.

Furthermore, a fuel phase, which may especially be  
20 methane, is injected axially through the abovementioned opening into the central zone, generally at a speed of approximately 100 to 150 m/s.

The fuel phase is ignited by any known means in the region where the fuel and the helical phase are in contact.

25           As a result, the flow imposed by the gases in the narrow passage takes place along a set of trajectories which coincide with families of generatrices of a hyperboloid. These generatrices are based on a group of circles, of small-sized rings situated near and below the narrow passage,

before diverging in all directions.

The mixture to be treated is next introduced in liquid form through the abovementioned pipe. The liquid is then broken up into a plurality of drops, each of them being  
5 conveyed by a volume of gas and subjected to a motion creating a centrifugal effect. The flow rate of the liquid is usually from 0.03 to 10 m/s.

The ratio of the quantity of proper motion of the helical phase to that of the liquid mixture must be high. In  
10 particular, it is generally at least 100:1 and preferably from 1000:1 to 10,000:1. The momenta at the narrow passage are calculated as a function of the entry flow rates of the gas and of the mixture to be treated, and of the section of the said passage. An increase in flow rates results in an  
15 increase in the size of the drops.

In these conditions the proper motion of the gases is imposed in its direction and its intensity on the drops of the mixture to be treated, which are separated from one another in the region of convergence of the two streams. The  
20 speed of the liquid mixture is furthermore reduced to the minimum needed to obtain a continuous flow.

The compound in solid form of the invention is obtained as the product of the spray-drying.

The invention also relates to a colloidal dispersion  
25 obtained by suspending or resuspending in water the dispersible compound of the invention.

The dispersion thus obtained consists of colloids whose hydrodynamic mean diameter, measured by quasielastic light scattering (QELS), is generally from 5 to 200 nm.

It should be noted that this colloid size may vary with time. Thus, freshly prepared dispersions will have, for example, a mean colloid diameter of from 5 to 60 nm, more particularly from 20 to 40 nm. In the case of older  
5 dispersions, for example aged two days or more, this diameter will, for example, be from 40 to 200 nm, more particularly from 80 to 160 nm.

The dispersion may exhibit an yttrium or holmium oxide concentration that can reach 1 mole/litre.

10 Its pH is close to neutrality and lies more particularly from 6.0 to 7.5.

Finally, the invention relates to the use of the dispersion obtained from the dispersible compound described above, for the production of a coating on a substrate.

15 This use is made in a manner which is known per se. For example, the substrates may or may not be preoxidized.

The deposition of the dispersion on the substrate may be carried out directly using the dispersion of the  
20 invention by employing conventional coating techniques, for example of the dipping or spraying type.

After the deposition has been carried out the substrate has an adherent layer at the surface, which makes it capable of being handled.

25 The substrate is subsequently heat-treated.

The heat treatment is generally carried out at a temperature of not more than 600°C. This temperature may be lower, for example not more than 400°C, depending on the nature of the substrates.

A thin layer of rare-earth oxide, with a thickness which is generally lower than  $0.1 \mu\text{m}$ , is thus formed on the substrate.

Examples will now be given.

5 EXAMPLE 1

Synthesis of the sol

Synthesis of a sol is performed as described in FR-A-2,620,437. More precisely, one litre of 2N acetic acid is introduced into a thermostated reactor and is heated to  
10  $70^{\circ}\text{C}$ .

Next, 180 g of high-purity yttrium oxide (4N) are added.

After 30 minutes' reaction a jump in pH from 3 to 6 is observed, and the solution is then allowed to age for a  
15 further 3 hours 30 minutes. The suspension is collected and centrifuged at 3500 rev/min and the supernatant is recovered. The characteristics of the sol are the following:

- particle size: 6 nm
- pH: 6.8
- 20 - concentration: 160 g/l as  $\text{Y}_2\text{O}_3$
- empirical formula:  $\text{Y}(\text{OH})_{1.7}\text{Ac}_{1.3}$

Spraying

200 ml of sol are spray-dried on a laboratory Büchi, with an entry temperature of  $245^{\circ}\text{C}$  and an exit temperature of  
25  $119^{\circ}\text{C}$ .

Thermal analysis of the powder shows a release of acetic acid from 25 to  $150^{\circ}\text{C}$  and then of  $\text{H}_2\text{O}$  from 150 to  $245^{\circ}\text{C}$ , and then a decomposition of acetate in two stages ( $245^{\circ}\text{C}$  -  $320^{\circ}\text{C}$ , then  $320^{\circ}\text{C}$  -  $397^{\circ}\text{C}$ ). After  $600^{\circ}\text{C}$  the product

obtained is yttrium oxide.

Redispersion

30 g of powder are stirred into 50 ml of water. The mixture obtained is completely clear. Centrifuging at 4500  
5 rev/min for 10 minutes gives a centrifuge pellet whose weight is lower than 1% of the weight of the starting powder.

The sol obtained has the following characteristics:

- particle size: 15 to 20 nm, 40 to 100 nm after 2

days

10 - concentration: 166 g/l

After ultracentrifuging for 12 hours at 50,000 rev/min the colloid proportion is higher than 77%.

EXAMPLE 2, COMPARATIVE

A starting sol is synthesized as in Example 1.

15 Instead of being spray-dried, it is dried in the oven or by freeze-drying. The two powders obtained are redispersed as in Example 1, in a concentration of 180 g/l of  $Y_2O_3$ . The liquid obtained is centrifuged at 4500 rev/min for 10 minutes.

After centrifuging, a considerable deposition is  
20 observed at the bottoms of the tubes in both cases. The supernatants are inspected using QELS. Only very little scatter is observed, which indicates that the material present is not a sol but a solution.

CLAIMS

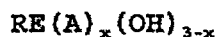
1. A compound in solid form, based on an yttrium or holmium hydroxide and on an anion of a monovalent acid which has a pKa of from 2.5 to 5.0, which compound is  
5 dispersible or redispersible in water in a proportion of at least 80% and predominantly in the form of a colloidal dispersion.

2. A compound according to claim 1, which is dispersible or redispersible in water such that at least 60%  
10 by weight is in the form of a colloidal dispersion.

3. A compound according to claim 2 which is dispersible or redispersible in water such that at least 75% by weight is in the form of a colloidal dispersion.

4. A compound according to any one of claims 1 to  
15 3 which has a particle size of not more than 10  $\mu\text{m}$ .

5. A compound according to any one of claims 1 to 4 which has the formula:



in which:

20 RE denotes yttrium or holmium,

A denotes the anion of the monovalent acid defined in claim 1; and

x is smaller than 2.5 and greater than 1.

6. A compound according to any one of claims 1 to  
25 5 wherein the monovalent acid is acetic acid.

7. A process for the preparation of a compound as defined in any one of claims 1 to 6 which comprises spray-

drying a colloidal dispersion based on an yttrium or holmium hydroxide and on an anion of a monovalent acid which has a pKa of from 2.5 to 5.0.

8. A process according to claim 7 wherein the  
5 colloidal dispersion is prepared by reacting an yttrium or holmium oxide with the acid and heating the reaction mixture obtained.

9. A colloidal dispersion obtained by suspending  
or resuspending a compound as defined in any one of claims 1  
10 to 6.

10. A colloidal dispersion according to claim 9  
which has a hydrodynamic mean diameter of the colloids from 5  
to 200 nm.

11. Use of a dispersion as defined in claim 9 or 10  
15 for the production of a coating on a substrate.

