EUROPEAN QUALIFYING EXAMINATION 2004

PAPER A
CHEMISTRY

This paper comprises:

LETTER FROM THE APPLICANT

Dear Sirs,

As you know, our company is interested in making compositions making use of gallium. For some time we have had a team working on the use of gallium and gallium alloys in particulate form as lubricants and now the results of this research are available. We ask you to file a European patent application covering this research based on the information provided in this letter. All matter worth patenting should be covered. In order to assist you in drafting the application(s), documents D1, D2 and D3, which in our opinion best illustrate the state of the art, are attached to this letter.

The melting point of gallium (29.8 °C) and of certain gallium alloys is extremely low and unlike other metals or alloys, they cannot be made into particles at elevated temperatures.

Use is made in the present invention of metallic gallium or alloys of gallium which have a melting point between 27 and 60°C. Such alloys typically contain at least one metal selected from the group consisting of zinc (Zn), indium (In), aluminium (Al) and tin (Sn). Examples of suitable gallium alloys are Ga-5Zn, Ga-15Zn, Ga-40In, Ga-5Al or Ga-15Al, wherein Ga-xM means an alloy consisting of 100 - x parts by weight (pbw) of gallium and x parts by weight (pbw) of metal M. For example Ga-5Zn defines an alloy consisting of 95 pbw of gallium and 5 pbw of zinc.

It has been observed that when a gallium alloy is used, the greater the content of gallium, the better are the gliding or lubricating properties of the composition containing particles of that alloy. The content of gallium in the alloy must be at least 50 wt% in order to ensure sufficient gliding and lubricating properties.

We use a process with which metallic gallium or the above defined gallium alloy is converted to fine particles of a diameter not larger than 500 µm and even to finer particles of a diameter not larger than 150 µm.

This process comprises the steps of

a) melting metallic gallium or a gallium alloy having a melting point between 27 and 60 °C in an atmosphere of inert gas such as nitrogen at a temperature not higher than 100 °C, preferably at a temperature in the range of 70 - 90 °C and

b) injecting the molten gallium or gallium alloy through a vibrating nozzle into a cooling medium. The cooling medium which may contain additives, is water or an aqueous solution. It is kept at a temperature not higher than 10 °C, preferably not higher than 5 °C, i.e. a temperature below the melting temperature of gallium or of the gallium alloys in order to ensure a rapid solidification of the droplets sprayed from the nozzle. The size of the particles is adjusted by varying the pressure applied for injecting the molten gallium or gallium alloy into the cooling medium.

The solidified gallium or gallium alloy particles settle to the bottom of the cooling medium and therefore can be easily separated from the cooling medium.

The process so far described is known from document D1.

The surface of the gallium or gallium alloy particles can be optionally coated with any known coating agent. The amount of coating agent usually does not exceed 5 weight percent (wt%) of the gallium or gallium alloy particles.

The gallium or gallium alloy particles can be coated after separation from the cooling medium using conventional coating methods. If the coating agent is a coupling agent or a surfactant (i.e. one of the coating agents we use for providing suspensions of gallium or gallium alloy particles in liquid media), it can be already present in the cooling medium as an additive, in which case gallium or gallium alloy particles coated with a coupling agent or a surfactant are directly obtained in step b) of the process described above.

Use of the particles:

The gallium and gallium alloy particles may be either dispersed in polymeric resins or, subject to certain conditions explained further below, suspended in liquid media. If a polymeric resin is used, a material containing the gallium or gallium alloy particles results which can be used to make a gliding surface. If a liquid medium is used, a liquid composition, such as an engine oil or liquid ski wax, containing the gallium or gallium alloy particles results.

The gallium or gallium alloy particles are preferably mixed in amounts of at least 0.05 parts (all parts to be designated hereinafter are based on weight) with 100 parts of the polymeric resin or liquid medium. The amount of gallium or gallium alloy particles to be used may vary depending upon their specific use, but is preferably not more than 5 parts of gallium or gallium alloy particles per 100 parts of resin or liquid medium in view of cost. It was established by experiment that using such small amounts of gallium or gallium alloy particles was sufficient to give good results. Moreover, the gallium or gallium alloy particles must be suspended in the liquid medium or uniformly dispersed in the resin composition to obtain sufficient lubricating and gliding properties.

Dispersions in polymeric resins:

As explained above the coated gallium or gallium alloy particles can be dispersed in polymeric resins , e.g. polystyrene, polyvinyl chloride, polyvinyl acetate, polyethylene or polypropylene using conventional techniques. When the gallium or gallium alloy particles are incorporated into polymeric resins, the coating agents in the amount indicated above do not affect the lubricating and gliding properties. The addition of uncoated gallium or gallium alloy particles to one of the above resins is also possible depending on the contemplated use of the resulting composition.

The resin compositions which contain the above gallium or gallium alloy particles exhibit high gliding properties on snow and water. They are therefore particularly suitable in the production of gliding surfaces for skis and motor boats.

Suspensions in liquid media:

The gallium or gallium alloy particles are, as explained above, also useful for making suspensions, i.e. they can be suspended in a liquid medium (i.e. a medium which is liquid at 20°C) as illustrated by alcohols, oils, lubricants and aqueous solutions. This however requires a diameter of the gallium or gallium alloy particles of not greater than 150 µm, preferably not greater than 50 µm. This furthermore requires the use of a coating agent selected from the group consisting of paraffin waxes, surfactants and coupling agents. The use of other conventional coating agents such as low molecular weight ethylene oxide polymers and low molecular weight propylene oxide polymers does not lead to stable suspensions.

A suitable paraffin wax is commercially available under the trade name Parawa surfactants used may be non-ionic, anionic, cationic or amphoteric. The surfactant preferably a fluorochemical, for example Fluorofact®. Coupling agents are compounds which have an organic functional group having affinity for organic materials and a hydrolysable group having affinity for inorganic materials and which are capable of chemically coupling organic and inorganic materials. Illustrative coupling agents are silane coupling agents such as those sold under the trade name Silacoupling.

The suspensions usually will be prepared by incorporating the above described coated gallium or gallium alloy particles into the liquid medium, which is to be selected according to the intended use. Preferred liquid media are engine oils or the solvents conventionally used for making liquid ski wax. The addition to a commercial engine oil of the above described coated gallium or gallium alloy coated particles reduces the consumption of gasoline, due to the lubricating effect of gallium. Liquid ski waxes obtained by using the coated gallium or gallium alloy particles have high performances on all types of snow.

The following examples are provided for the purpose of further illustrating the present invention.

In each of the examples described below, the content of gallium or gallium alloy particles was adjusted to be 0.5 wt% of the total amount of liquid medium or polymeric resin. The amount of coating agent if any is adjusted to be 1.0 wt% of the amount of gallium or gallium alloy.

Example 1

A gallium alloy of composition Ga-5Zn, i.e. consisting of 95 pbw of gallium and 5 pbw zinc was melted under a nitrogen atmosphere and injected into cold water to obtain fine particles of gallium alloy having a diameter below 50 µm. The resulting particles were separated from the cooling medium and mixed with a fluorochemical surfactant. The particles coated with the fluorochemical surfactant were then added to an engine oil so as to prepare a liquid suspension of gallium alloy particles.

This suspension was used as automotive engine oil and the consumption of gasoline was about 15% less than when a commercial engine oil was used, due to the lubricating effect of the gallium alloy.

Tests were repeated in the same manner as above except that particles of gallium alloy having a composition of Ga-15Zn, Ga-40In, Ga-5Al or Ga-15Al were used instead of particles having a composition of Ga-5Zn. In each run a similar advantageous result was obtained.

Example 2

Uncoated gallium alloy particles of composition Ga-5Zn were produced according to the procedure used in the first step of above example 1. The particles (diameter below 50 µm) were separated, dried and added to a mixture of toluene and paraffin wax. The mixture was heated to evaporate the toluene. The particles coated with paraffin wax were added to an organic solvent (n-hexane) and the solution was cooled for 30 minutes to make a gallium alloy particle containing suspension. This suspension proved to be very effective for waxing skis.

Tests were repeated in the same manner as above except that particles of gallium alloy having a composition of Ga-40In, Ga-5Al or Ga-15Al were used instead of particles having a composition of Ga-5Zn. In each run a similar suspension effective as a liquid ski wax was obtained.

Example 3

Metallic gallium was melted and injected into cold water to obtain particles of gallium having a diameter below 100 µm. These uncoated particles were separated, dried and added to polypropylene. The uniform mixture obtained provided a surface with excellent gliding properties. Tests were repeated in the same manner as given above except that particles of gallium alloy having a composition of Ga-15Zn, Ga-40In or Ga-15Al were used instead of particles of metallic gallium. In each run each of the mixtures obtained had excellent gliding properties.

Example 4

Metallic gallium was melted and injected into cold water containing a silane coupling agent to obtain particles of gallium having a diameter below 100 µm. The particles coated with the silane coupling agent were separated, dried and added to polyethylene. The mixture obtained provided a uniform surface with excellent gliding properties on water.

Tests were repeated in the same manner as given above except that particles of gallium alloy having a composition of Ga-15Zn, Ga-40In or Ga-15Al were used instead of particles of metallic gallium. In each run each of the mixtures obtained had excellent gliding properties.

As shown in the above Examples 1 through 4 gallium particles which can be used in the present invention include particles of gallium alloys as well as particles of metallic gallium. Almost equal satisfactory results can be obtained by using particles of gallium alloys or particles of metallic gallium. The reason for this has not been fully clarified yet. Probably, the characteristic properties of gallium inclusive of excellent lubricity, wear resistance and gliding properties can be fully displayed even in the form of alloy particles because the diameter of the particles is extremely small, i.e. not larger than 500 µm. It is also interesting to note that the gliding performance of the resin composition does not depend on the type of coating agent used.

DOCUMENT D1 (State of the art)

Title: Method of producing particles of metallic gallium and its alloys

This process comprises the step of a) melting metallic gallium or a gallium alloy having a melting point between 27 and 60 °C in an atmosphere of inert gas such as nitrogen at a temperature not higher than 100 °C, preferably at a temperature in the range of 70 - 90 °C and b) injecting the molten metal through a vibrating nozzle into cold water (temperature below 10 °C, preferably below 5 °C), optionally comprising ethanol, leading to solid particles having a diameter not larger than 600 µm, preferably not larger than 50 µm. The size of the particles is adjusted by varying the pressure applied for injecting the molten metal into the cooling medium. The gallium or gallium alloy particles obtained settle to the bottom of the cooling medium and therefore can be easily separated from the cooling medium. The gallium alloy may comprise metals selected from indium (In), zinc (Zn), aluminium (Al), cadmium (Cd), scandium (Sc) or tin (Sn). The content of indium, zinc, aluminium, cadmium, scandium or tin in the alloy is preferably less than 50 parts by weight (based on 100 parts by weight of gallium alloy) in order to achieve a proper melting of the alloy. The present process has been shown to be very efficient for providing metallic gallium particles and particles of alloys having the following formulae Ga-5Zn, Ga-15Zn, Ga-40In, Ga-5Al or Ga-15Al, where Ga-xM means an alloy consisting of 100 - x parts by weight (pbw) of gallium and x parts by weight (pbw) of metal M.

DOCUMENT D2 (State of the art)

Title: Gliding surface material

A material for a gliding surface is obtained by uniformly dispersing in a synthetic resin 0.01-5 weight % (wt%) based on the weight of the synthetic resin of gallium alloy particles. The particles may be coated with a coating agent, preferably in an amount up to 5 wt% based on the weight of the particles. Preferred coating agent is a low molecular weight ethylene oxide polymer, although any known coating agent will provide equivalent gliding properties. The diameter of the gallium alloy particles is preferably up to 500 µm, more preferably up to 150 µm and most preferably up to 50 µm. Suitable resins for the composition include polystyrene, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, poly(meth)acrylic acid and its salts and esters, polyacrylamides, polyethylene, polypropylene, polycarbonate, polyphenylene sulphide, polybutadiene or polychloroprene. Suitable alloys for the present composition are of formula Ga-xM, wherein Ga-xM means an alloy consisting of 100 - x parts by weight (pbw) of gallium and x pbw of metal M. x is up to 50 and typically ranges from 1 to 30. Examples of gallium alloys are Ga-10Zn, Ga-20In, Ga-50In, Ga-10Al, Ga-15Al, Ga-30Sn and Ga-50Sn. It was shown that gallium alloy particles dispersed in solid resin compositions provide high gliding properties to said resin compositions. The compositions due to the lubricating effect of the gallium can be formed into gliding surface materials having water repellency, wear resistance and high gliding performance on water, snow or ice. They are therefore suitable for providing motor boat, snow board or ski gliding surfaces.

DOCUMENT D3 (State of the art)

Title: Surfacing material for the gliding surface of a ski

A material which comprises: A) a polymeric resin, in particular a polyolefin type resin such as polyethylene or polypropylene, and B) from 0.01 to 5 wt% based on the polymeric resin of particles of metallic gallium dispersed uniformly in said polymeric resin is particularly useful for the production of a surfacing material for a ski. At snow or ice temperature, the gallium particles expand, and as the result of their expansion, gallium particles are held strongly enough on the gliding surface of a ski to maintain good water-repelling and glide characteristics over a prolonged period without allowing the gallium particles to come off the ski. The composition is also useful for many other similar uses such as a plastic gear, a constructional material, a marine structural material and the like because of its excellent glide, water-repelling and wear resisting properties, which can be retained for a prolonged period. For the above similar uses, the polymeric resin can be selected from cellulose acetate, polyamide, polystyrene, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene and polycarbonate. The gallium particles are optionally covered with a coating agent (preferably a low molecular weight propylene oxide polymer, although any known coating agent will provide equivalent gliding properties) usually in an amount up to 5 wt% based on the particles weight. The gallium particles preferably have a diameter up to 500 µm, more preferably up to 150 µm and most preferably up to 50 µm.