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## Candidate's Answer

Ga and Ga alloy particles and uses thereof

Technical field

The invention concerns the use of Ga and Ga alloys in lubricant compositions.

Background of the invention

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

~~Use is made in the present invention~~ From D1 it is known to form particles 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. Such particles have lubricant qualities (see D2 and D3).

*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~~ From D1 is known a process with which metallic gallium or the above defined gallium alloys can be converted to fine particles of a diameter not larger than 500 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.*

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- 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.*~~

*As disclosed in D2 and D3 the surface of the gallium or gallium alloy particles can be optionally coated with any known agents. The amount of coating agent usually does not exceed 5 weight percent (wt%) of the gallium or gallium alloy particles.*

From documents D2 and D3 it is known to use Ga or Ga alloy particles to form resin lubricants, by incorporating coated or uncoated Ga or Ga alloy particles into a polymeric resin. Such resin lubricants are said to be useful as surfacing materials for skis and for gliding surfaces of motorboats.

It would be desirable to have liquid suspensions of Ga or Ga alloy particles, for example, for use in engine oils. Unfortunately the coating agents used in the prior art propylene oxide (D3) and low molecular weight ethylene oxide polymers (D2) do not lead to stable liquid suspensions. A need remains for particles of Ga or Ga alloy suitable for the formation of liquid suspensions. Such liquid suspensions would be expected to have useful lubricant properties.

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## Summary of the invention

In a first aspect the invention provides (claim 1).

In a second aspect the invention provides a process for making the particles of the invention comprising the steps (see claim 5).

In a 3<sup>rd</sup> aspect, the invention provides the use of the particles of the invention for the manufacture of a liquid suspension lubricant.

In a 4<sup>th</sup> aspect, the invention provides a liquid suspension comprising the particles of the invention suspended in a medium liquid at 20°C.

In a 5<sup>th</sup> aspect, the invention provides an engine oil comprising the particles of the invention.

In a 6<sup>th</sup> aspect, the invention provides a liquid ski wax, comprising the particles of the invention.

## Detailed description

The inventors have surprisingly found that when Ga or Ga alloy particles are coated with a coating agent selected from the group consisting of paraffin wax, a surfactant and a coupling agent, particles are obtained that are suitable for forming stable suspensions. The Ga or Ga alloy particles may be made by known processes, to have a diameter of not greater than 150 µm.

*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 coupling agent or a surfactant are directly obtained in step b) of the process described above.*

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*Use of the particles:*

*The gallium and gallium alloy particles may be either dispersed in polymeric resins as in the prior art 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 as known from D2 and D3. If a liquid medium is used, a liquid composition, such as 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 disclosed in D2 and D3 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.*

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### *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 as disclosed in D2 and D3 does not lead to stable suspensions.*

*A suitable paraffin wax is commercially available under the trade name Parawax. The surfactants used may be non-ionic, anionic, cationic or amphoteric. The surfactant is preferably a fluorochemical, for example Fluorofact<sup>®</sup>. 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.*

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### Example 1

*A gallium alloy of composition Ga-5Zn, i.e. consisting of 95 pbw of gallium and 5 pbw of zinc was melted under a nitrogen atmosphere and injected into cold water to obtain fine particles of gallium alloy having a diameter below 50  $\mu\text{m}$ . 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  $\mu\text{m}$ ) 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.*

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*Example 3 (conventional resin process)*

*Metallic gallium was melted and injected into cold water to obtain particles of gallium having a diameter below 100  $\mu\text{m}$ . 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 (new process eliminates 1 step from prior art of D1 or D2 non-unitary, since inventive step is different: elimination of step.*

*Metallic gallium was melted and injected into cold water containing a silane coupling agent to obtain particles of gallium having a diameter below 100  $\mu\text{m}$ . 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  $\mu\text{m}$ . It is also interesting to note that the gliding performance of the resin composition does not depend on the type of coating agent used.~~*

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Note to examiner: Although the resin composition of Example 4 is novel (D2 and D3 do not disclose a silane coating agent), inventive step would be difficult to argue, since we are told that “the gliding performance of the resin composition does not depend on the type of coating agent used” , and the addition of the Ga or Ga alloy particles for the resin does not depend on a coating step. There is no apparent advantage to the use of silane as coating agent when the particles are incorporated into a resin.

Claims:

1. Particles of gallium or gallium alloy having the following characteristics: at least 50% by weight of gallium content, a diameter not larger than 150  $\mu\text{m}$ , wherein the particles are coated with a coating agent selected from the group consisting of paraffin wax, a surfactant, and a coupling agent having an organic functional group having affinity for organic materials and a hydrolysable group having affinity for inorganic materials and capable of chemically coupling organic and inorganic materials.
2. Particles according to claim 1, wherein the diameter is not larger than 50  $\mu\text{m}$ .
3. Particles according to claim 1 or 2, wherein the coating agent does not exceed 5 wt% of the Ga or Ga alloy particles.
4. Particles according to claim 1, 2 or 3, wherein the coating agent is selected from the group consisting of Parawax, a fluorochemical, and a silane coupling agent.
5. A process for making particles according to any one preceeding claim, comprising the steps:
  - a) melting metallic gallium or a gallium alloy having a melting point between 27 and 60°C in an atmosphere of inert gas, at a temperature of not higher than 100°C,
  - b) injecting the molten gallium or gallium alloy through a vibrating nozzle into a cooling medium of water or an aqueous solution, kept at a temperature of not higher than 10°C, adjusting the size of the particles to a diameter of not larger than 150  $\mu\text{m}$  by adjusting the pressure applied for injecting the molten gallium or gallium alloy into the cooling medium,

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- c) separating the solidified particles from the cooling medium, and
  - d) coating the particles with a coating agent selected from the group consisting of paraffin wax, a surfactant and a coupling agent as defined in claim 1.
- 6. A process according to claim 5, wherein the coating agent is selected from a surfactant or a coupling agent, and step (d) is performed simultaneously with step (b) by having the coating agent present in the cooling medium.
  - 7. Use of the particles of any one of claims 1-4, for the manufacture of a liquid suspension lubricant.
  - 8. A liquid suspension comprising the particles of any one of claims 1-4 suspended in a medium liquid at 20°C.
  - 9. A liquid suspension according to claim 8, wherein the liquid medium is selected from the group consisting of alcohols, oils, lubricants and aqueous solutions.
  - 10. An engine oil comprising the particles of any one of claims 1-4.
  - 11. A liquid ski wax comprising the particles of any one of claims 1-4.
  - 12. A process for making the liquid suspension of claim 8, comprising incorporating the particles of any one of claims 1-4 into the liquid medium.
  - 13. A process for making the engine oil of claim 10, comprising incorporating the particles of any one of claims 1-4 into an engine oil.
  - 14. A process for making the liquid ski wax of claim 11, comprising incorporating the particles of any one of claims 1-4 into a solvent used for making liquid ski wax.

**The following claims are non-unitary, and could be divided out after filing:**

- 15. A process for making a lubricating resin composition, comprising the process of claim 6, (eliminates a step from the prior art) followed by dispersing the coated particles in a polymeric resin.