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(54) Title: COMPOUND TO PRODUCE CONDUCTIVE CIRCUITS

(57) Abstract: To improve the characteristics of a compound containing a polymer dispersion polarisable by an electromagnetic or electrical field having electric resistivity, from insulator to conductor and vice versa, modifiable by said field, the polymer comprising PATAC.



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## COMPOUND TO PRODUCE CONDUCTIVE CIRCUITS

The invention relates to a compound, to be spread for example on any surface, in which to carry out conductor circuits and/or electrical charge generators, in the form of a signal or  
5 current. The compound can be modified by an electromagnetic field to vary its electrical conductivity.

In WO2011125037, herein referred to, a paint or compound is described, which can be polarised for example by means of a laser, in which polymers and dopants have been  
10 dispersed so as to give it electrical properties. The compound contains a polymer with a double covalent conjugated bond, Thiophene, which when illuminated by Laser is able to modify its electrical conductivity.

During the experiments the problem of improving the characteristics of the compound was  
15 addressed.

The invention sets out to overcome this problem with the compound defined in claim 1. The compound has a specific structure which makes its polarisation and de-polarisation easy and reliable so as to selectively create within it conductor or insulation paths or zones.  
20 In particular, compared to Thiophene PATAC has the advantage of having a different configuration of the free radical which a Laser can oust to make the polymer conductive. When the radical is ousted by the Laser, the PATAC becomes more conductive than the Thiophene. In addition, the PATAC is easier to polarise with a Laser at 488 nm, commonly found in labs or for sale.

25

PATAC belongs to the family of polyacetylenes, and represents a generic family of photopolymers which require only laser exposure to become electrical conductors by breakage of the lateral thioalkyl chains. PATAC appears as a brown powder, soluble in everyday aromatic solvents. After laser exposure, the zones struck lose part of the thioalkyl  
30 lateral chains and a blue-black, insoluble and conductor polymer is then obtained. PATAC is also a polymer with double covalent conjugated bond, that is to say a heterocyclic compound, formed of n atoms of carbon and one atom of a different type (or radical) linked

in a loop structure.

The choice of the type of luminous stimulus to use is important since too bland a stimulus is not sufficient to break the carbon-sulphur bonds, while an overly energetic stimulus gives rise to a form of pyrolysis which gives an insulating material. The preferred laser for striking the PATAC is a laser with a wavelength of 488 nm.

The compound can be applied in liquid or gel form directly to a medium or applied by means of a separate film or rigid or flexible support layer.

10

The compound according to the invention also makes it possible to exploit the electrical specifications for the generation of electricity or mechanical vibrations, see below.

Note that the compound preferably contains in dispersion all the elements which we will describe as inside a generic solvent, preferably aromatic. In particular, the use of a benzene is preferred, and preferably a dichlorobenzene (because it dissolves the PATAC or Thiophene well), a dichloromethane or nitro-type diluent.

15

The PATAC and any one of the elements described below (even if cited in preferred combinations) is dispersed in the solvent.

20

The compound can then be spread or sprayed onto any surface. It can comprise metallic oxides which are useful since they make electrons available in the matrix /compound.

25

As well as metal oxides there can be a further component for example such as a graphite or graphene which are excellent dopants, above all on account of their elevated electrical conductivity. They also give the compound the property of being oily, that is of always maintaining a certain fluidity, without ever drying. Particular graphite sub-families which have proven extremely advantageous, because said qualities are accentuated, are fullerene and graphene.

30

Ferric chloride or aluminium chloride, with or without colouring pigments, may be added to the metallic oxides plus PATAC. Such chlorides are highly doping, and are convenient

both because they eliminate a hysteretic phenomenon and because they have a marked ability to release/accept electrons. In particular, the ferric chloride or aluminium chloride are oxides dissolved in chlorine which dissolve well in the PATAC, which is a plastic. The excellent homogenisation ensures optimal communication at an electronic level, favouring  
5 the interchange of electrons towards the PATAC.

The metal oxides may, for example, be composed of iron oxides in the formulation  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  or even better, for their improved magnetisation/saturation curve, of chrome oxides or dioxides, in the formulation  $\text{CrO}_2$ .

10

The metallic oxides, with any graphite, and the PATAC are dispersed in the matrix of paint in proportionate quantities to the type of current or electrical signal which said paint must conduct.

15 The compound is struck with a Laser or other electromagnetic radiation to energise or de-energise the PATAC molecules sending the right energy. When they are energised their electronic status changes and they become conductors. A subsequent radiation pours energy onto the energised molecule and returns it to its original electronic configuration, that is to say, an insulator. In particular, the Laser radiation breaks the bond of the radical  
20 in the PATAC containing sulphur, leaving the polymer chains of PATAC in reciprocal electronic and conductive contact through the free orbital. A subsequent radiation reconstitutes the bond with the free radical and/or disconnects the chains of PATAC again, and at that point the compound becomes an insulator once again.

25 Clearly the Laser can be used to create conductive zones or paths in the compound as desired.

It is preferable to have affine elements for the PATAC, atomically very close, which trap the ousted electron and return it to the polymer when the energy of anti-polarisation arrives  
30 (the molecule of the polymer is therefore functionalised by the affine element).

An element suitable for such purpose is quartz, but other materials may be used for such

purpose.

In particular, the compound may be loaded with PATAc and a quartz-based filler (one or more of its 19 families), in particular BaTiO<sub>3</sub> or PbTiO<sub>3</sub>. A component with TiO<sub>3</sub> has the advantage of being very adhesion-effective, does not dry and is able to make free electrons available with little energy.

In the compound, quartz of different particle sizes is preferably dispersed, both to carry charges towards the PATAc and to promote the changes of the energised state, both as voltage/current generator by piezoelectric effect. In fact a thrust of an object on the compound generates a discharge or impulse of current in the quartz. By pressing and releasing the compound periodically a pulsating current is generated. Such current may be collected by one or more paths of PATAc made conductive. A surprising consequence is that vibration-generating areas can be designed at will on the paint (by means of polarisation). Alternatively, or additionally, the vibration can be activated in areas chosen at will by having an electrical energisation available for the quartz.

It is not easy to disperse sintered material in a matrix or compound containing quartz, so-called "loaded" quartz, in other words provided with micro-electrodes, preferably metallic, to collect or send electrical charges. A process for loading quartz involves sublimating two conductor sheets above and below a layer of quartz at high temperature (about 700°C), sintering it at 1000°C and then cooling it to about 200°C before exposing it to an electric field of about 3000V/cm so as to position all the quartz particles with the electrodes parallel and alongside each other. A sandwich structure of oriented quartz placed between two conductor sheets results.

An inventive solution envisages that such sandwich is ground to form small particles of quartz as desired which each have two electrodes. The particles are then dispersed in the compound.

Another problem is the orientation of the particles of loaded quartz. Especially when the quartz generates charge impulses following a charging or pulsating force, the maximum

energy yield is only achieved if the quartz is oriented parallel to the direction of the pulsating force. That is to say that the micro-electrodes of each particle of quartz should align with the line of action of the force, so as to receive the maximum component. In addition, each application may require different orientations. For example, if the charging force is a vehicle and the compound is spread on the road, it is clear that the quartzes should preferably be inclined in relation to the orthogonal of the road surface, towards the oncoming vehicle. Only thus is the component resulting from the movement impressed on the component exploited.

10 The sintering method described above may at most produce quartz dispersed in a compound which has two electrodes, the axis of which is oriented substantially orthogonal to the main surface of the compound.

The invention sets out to overcome this problem by means of an original method. Not only does the use of a magnetic field enable orientation of all the quartz particles in whatever direction desired, but this happens even at very low temperatures, e.g. max 150°C, at which the compound is still in a gelatinous form and not dry, and does not risk deterioration as a result of the high temperature. Note that the prior art with electrical field, applied rather to a solid sandwich and not to a fluid compound, requires heating to a high temperature of the material, with problems of deterioration. The axis of the quartz particle can be oriented at will by simply directing the magnetic field in the desired direction. The quartz particles are floating in the compound yet to solidify and rotate to orient themselves without much opposition.

It is, anyway, possible to use both the methods expounded above, either separately or combined.

An alternate magnetic field generated for example with an inductor coil, at frequencies for example to the order of KHz or static magnetic fields generated by magnetic dipoles, is more advantageous because it periodically induces an orienting momentum on the particles and, period after period, succeeds in orienting the quartz without stress on the material.

To definitively stabilise the configuration of the particles of loaded quartz, one simple and

efficacious way is to expose the compound to UV radiation. As UV the general type used, for example to dry paints, may be used.

Substantially the invention relates to a method for inserting or dispersing quartz inside a  
5 compound containing PATAC or Thiophene or a polymer polarisable by an electromagnetic field having electric resistivity, from insulator to conductor and vice versa, modifiable by an electromagnetic field or Laser, in which particles comprising two conductor layers and one layer of quartz in the middle are dispersed in the compound.

10 Preferably a sintered material, comprising in a sandwich structure two conductor layers and one quartz layer in the middle, is ground to obtain said particles.

Preferably the particles of quartz dispersed in the compound are oriented spatially by means of a magnetic field, where preferably the magnetic field is an alternate magnetic field.

15

One way of exploiting the magnetic field as an orienting stimulus of the quartz is to include in said sandwich structure an element (dopant) sensitive to a magnetic field or a magnetic element (dopant). The element may be in nanometric form such as powder, particles or atoms.

20

The sensitive element is preferably inserted in said sandwich structure by means of diffusion, making the sensitive element migrate into the quartz. The migration may preferably determine that the diffused element attaches itself superficially to the quartz.

25 Another preferred system is to join/fasten said sensitive element mechanically to said structure, for example chemically.

Said magnetic field sensitive element, or element (dopant) capable of being magnetised, may for example be iron or iron powder or a powder magnet.

30

It is preferable for said element to already have a magnetic polarity, that is a north and south magnetic pole so that the quartz orientation is more accurate.

To favour the orientation of the element and therefore of the associated quartz, under the effect of the magnetic field, it is preferable for it to have an elongated shape such as a nanometric stick, so that it can orient itself along the lines of the field.

- 5 Note that the particle comprising two conductor layers and a quartz layer in the middle in a sandwich structure, and a magnetic element associated to such structure offers all the advantages which can be obtained from the piezoelectricity of the quartz and the possibility to orient it spatially inside the compound by mean of a magnetic field in a molasses form.
- 10 The said particle may be used in any type of compound which can exploit its piezoelectric and/or spatial orientation abilities.

Preferably the compound is exposed to UV radiation to fix the spatial position of the particles.

15

To further increase the conductivity of the compound when it is conductive the PATAC (or Thiophene) is loaded with aggregating gents such as Ag, Ni, St, Au or Pt.

- For example, the PATAC goes from about  $2M\Omega/cm^2$  to about  $100\Omega/cm^2$  by means of
- 20 Laser radiation. Silver, or one out of Ni, St, Au or Pt, has given optimal conductivity results, lowering the resistance by orders of magnitude. The silver replaces the sulphur atom lost by the PATAC or Thiophene in the compound during polarisation by Laser, and creates a conductive bridge between the molecules of PATAC (or Thiophene). The percentage in volume of silver in the compound is preferably 6% to 14 %. Below these
- 25 values it does not have the desired effect and above, it damages the Thiophene or PATAC molecule. Compounds such as Carbon Black, and/or components of carbon black and/or carbon nanotubes may be added for the same functioning goals.

- The phenomenon behind the improvement is as follows. When the laser locally illuminates
- 30 the PATAC to make it conductive it heats the surrounding area, creating a "molten pool". An element like silver has a much higher specific gravity than the PATAC and migrates towards the PATAC by temperature gradient, increasing its conductivity.

Preferred percentages in weight of the compound are:

- 4-8% of Silver, preferably 6%,
- 85-95% of solvent, preferably 90%, and
- 3-5% of PATAC, preferably 4%.

5

The compound may be struck by a magnetic (and/or electrical field) to orient the quartz thereby preventing it from making elements other than the quartz migrate or shift. The aforesaid materials are non-magnetic and are not influenced by the magnetic field.

- 10 One unforeseen problem which the applicant encountered is the damage to the polymer chains caused by the steam which the substrate may absorb by exposure during the application.

Whether making a painted layer or during spraying the paint inevitably comes into contact  
15 with the atmosphere. The paint applied or in flight may therefore contain or absorb within it molecules or nanoparticles of water. From a microscopic point of view not only do such molecules constitute gigantic obstacles for the chains to be polarised, but they may also expand as the temperature rises and thereby break the molecular chains already formed. It is clear that the physical properties and industrial characteristics of the substrate are greatly  
20 jeopardised by this phenomenon. Having to operate in highly controlled surroundings or a vacuum is undesirable both because the production costs are every high and because any use by non specialised operators is precluded.

The invention intends to resolve this problem by adding a humidity acceptor to the compound so as to absorb the molecules of water and keep them in fixed areas of the  
25 substrate.

If the substrate is not yet dried and/or the solvent evaporated, the acceptor is able to capture the water molecules floating in the substrate and attract them towards itself, for example by spontaneous migration and /or a strong chemical affinity. It follow that the various molecules which scattered throughout the substrate could randomly damage the structure  
30 aggregate permanently in isolated points and leave a high percentage of free space fully polarisable.

A zeolite in the form of a salt or paste remaining inert in the absence of water and not creating any problem in the substrate, may be used as the acceptor. Iodine may also be used a humidity acceptor and offers the following advantages: It can be introduced as gas or liquid, adding it to the substrate while still damp, thereby adapting to any type of  
5 deposition method. Iodine is a conductor and may therefore be used to increase the conductivity of the substrate and is also of limited cost.

Another concept of the invention relates to a polarisation method of a volume of substrate material containing the polarisable molecules of PATAC. An electromagnetic radiation  
10 capable of creating an active zone able to locally supply the energy needed to vary the state of polarisation of a molecule such as PATAC and therefore its conductivity to create or cancel conductive paths is sent into the substrate.

To polarise a chain of PATAC molecules the relative position of the active zone and the  
15 volume may be varied (that is to say the active zone is moved and the volume is fixed or vice versa, or both are relatively mobile), and the relative position varied along three Cartesian axes. In other words the active zone can polarise a chain of molecules which has any two end points in space of the volume and three-dimensional extension desired between these points.

20

For reasons of accuracy and practicality it is preferable to control the radiation to move the active zone in relation to the fixed volume.

25

In particular, it is useful to use two or more Laser rays converging in a point, so as to create the active zone in such point. The advantage being that a certain specific power can be transferred to a point of the polarisable material by dividing it among a number of rays (the fractioned power of each ray is then summed in the active zone). This way the layers between the active zone and the laser source, which are inevitably exposed to the greatest power of each laser ray, are not burnt or altered.

30

By having two or more Laser energy conveyors, the angle of convergence (flat or cone-shaped) of the rays in said point may be varied to modify the spatial position of the point

(that is of the active zone). If the laser sources are at a fixed distance from the volume, then it is sufficient to vary the direction of each Laser ray as needed to make them collimate in the desired point.

- 5 In the case, for example, in which the polarised molecules of PATAc form conductive paths in the volume, the non-polarised condition corresponds to behaviour as an electrical insulator.

10 It is very useful to be able to connect the paths to connectors or direct sockets (for example using conductive glues) to external electrical terminals or pins. To make the path ends available outside the volume a chain of PATAc molecules can be polarised to make it extend from a certain depth of the material, where the chain forms a path ( e.g. flat) up to a more external ( visible) surface of the material , where the path can be contacted to pick up or emit a signal .

15

Complex electrical circuits require sophisticated and multilevel unravelling. A molecule chain may be polarised so as to make it extend around the longitudinal axis of another molecule chain polarised previously to create junctions on staggered planes for the paths or turns or bypasses. The pre-existent chain (or path) is bypassed without interrupting the  
20 electrical continuity of the new path.

Several paths can be joined easily by means of polarisation, or a common node created of the sum signal. To do so a molecule chain is polarised so as to make it extend until it touches another previously polarised chain. The point or node common to both chains is  
25 the sum node. Should it be desirable to connect or “sum” a path to another already existing along a section common to the connected paths, action may be taken to prevent the unwanted cancellation of paths, to inhibit the action of the active zone after the molecule chain currently in polarisation has touched the existing chain.

## CLAIMS

1. Compound containing a dispersion of polymers polarisable by an electromagnetic or electrical field having electric resistivity, from insulator to conductor and vice versa,  
5 modifiable by said field, characterised by the fact that the polymer comprises PATAC.
2. Compound according to claim 1, comprising a solvent which the dispersion is immersed in.
- 10 3. Compound according to claim 2, comprising as a solvent a benzene or dichloromethane.
4. Compound according to claim 1, 2 or 3, comprising ferric oxide or chrome oxides or dioxides.
- 15 5. Compound according to any of the previous claims, comprising graphite or graphene.
6. Compound according to any of the previous claims, comprising ferric chloride or aluminium chloride.
- 20 7. Compound according to any of the previous claims, comprising quartz particles.
8. Compound according to any of the previous claims, comprising particles comprising in a sandwich structure two conductive layers and one quartz layer in the middle.
- 25 9. Compound according to claim 8, wherein said sandwich structure comprises an element or dopant sensitive to a magnetic field or a magnetic element.
9. Compound according to any of the previous claims, comprising particles of Ag, Ni, St, Au or Pt.
- 30 10. Compound according to any of the previous claims, comprising particles of Carbon Black and/or carbon nanotubes.

11. Compound according to any of the previous claims, comprising in weight 4-8% of Silver, 85-95% of solvent and 3-5% of PATAC.

# INTERNATIONAL SEARCH REPORT

International application No PCT/IB2011/055194
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
INV. H05K3/10 H05K1/02 C09D5/23 C09D5/24 H01B1/24 C08L65/00 H01B1/12		
ADD. According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) H05K C09D H01B H01F B62D H01L G06K C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2011/125037 A2 (SPF LOGICA S R L [IT]; CAPPELLI FABIO [IT]) 13 October 2011 (2011-10-13) page 2 - page 10; claims 1-25 -----	1-11
X	H.-K. ROTH ET AL: "Electronic properties of laser modified poly(bis-alkylthio-acetylene)", SYNTHETIC METALS, vol. 101, no. 1-3, 1 May 1999 (1999-05-01) , pages 832-833, XP55030455, ISSN: 0379-6779, DOI: 10.1016/S0379-6779(98)01236-3 Experimental ----- -/--	1-3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
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"P" document published prior to the international filing date but later than the priority date claimed		
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Information on patent family members

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