

ORIGINAL

ABSTRACT

Title: A hybrid ink consisting of inorganic nanoparticles dispersed organic material and a method for preparing the same.

A hybrid ink formulation comprising: PVA and TiO_2 in a ratio of 10:1 in DI water and a method for preparing the same.

WE CLAIM:

1. A hybrid ink formulation comprising: PVA and TiO_2 in a ratio of 10:1 in DI water.
2. The hybrid ink formulation as claimed in claim 1 has dielectric constant in the range of 10.2 - 17.9.
3. The hybrid ink formulation as claimed in claim 1 wherein the capacitor is approximately 115.29 nF/cm^2 .
4. A method of making a hybrid ink formulation comprising:
dissolving TiO_2 solution in DI water separately,
dissolving PVA is also in DI water,
mixing the individual solution at room temperature.
5. The method as claimed in claim 4, wherein PVA is dissolved in DI water under stirring for 11-14 hours at $70^\circ - 90^\circ\text{C}$.
6. The method as claimed in claim 5, wherein PVA is dissolved in DI water under stirring preferably for 12 hours at 70°C .

Dated this 12th day of April 2012



OF L.S.DAVAR & CO
APPLICANTS' AGENT

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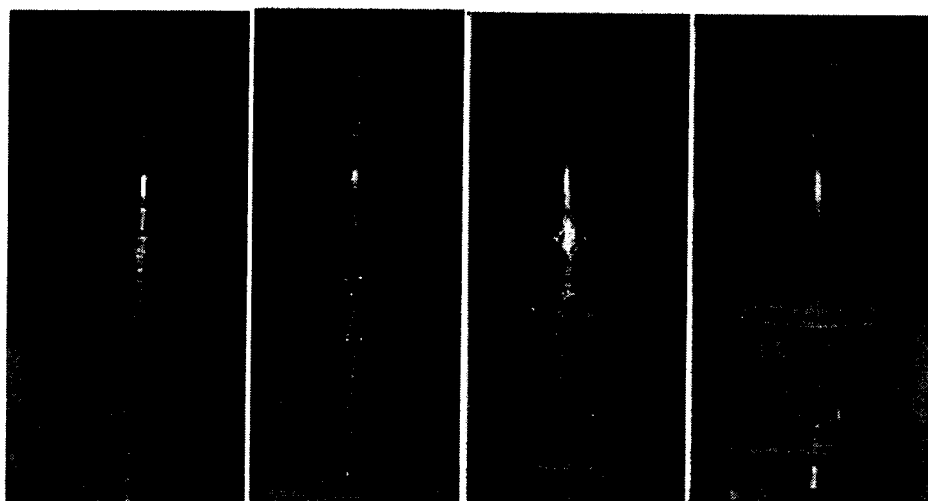


Fig 1: Photograph of TiO_2 incorporated PVA solution which was made of Approach 1, 2, 3 & 4

L. S. DAVAR & CO.
APPLICANTS' AGENT

Title: A hybrid ink consisting of inorganic nanoparticles dispersed organic material and a method for preparing the same.

FIELD OF INVENTION:

This invention relate to a hybrid ink formulation and a method for preparing the same.

BACKGROUND OF THE INVENTION:

One of the important inventions of 20th century is silicon based semiconductor technology – that revolutionized the microelectronics industry. But, there are some limitations of this technology. In large area electronic applications, silicon technology fails to deliver, e.g. flexible, transparent and low cost electronics – such as flexible displays, smart cards, RFID tags, electronic paper and other consumer electronics. Combination of organic electronics and printing technology provides that solution, but the challenge is in inventing new functional ink.

“Low-voltage organic thin-film transistors with polymeric nanocomposite dielectrics”, Organic Electronics 7 (2006) 435–439

Poly-Vinyl Phenol (PVPh), poly (melamine-co-formaldehyde) (PMF) methylated and titanium dioxide (TiO₂) nanoparticles were dispersed in organic solvent PGMEA. But dielectric constant increased only from 3.5 to 5.4 due to less solubility of TiO₂ in organic solvent. Then organosiloxane has been used to modify the surface of TiO₂ nanoparticles and increase the solubility of TiO₂ in organic solvent was improved to 15 wt%. After modification TiO₂ surface, a dielectric constant around 11 has been achieved.

“High-performance poly(3-hexylthiophene) top-gate transistors incorporating TiO₂ nanocomposite dielectrics”, Organic Electronics 11 (2010) 81–88

Further, higher percentage of TiO₂ was used in PVPh-TiO₂ nanocomposite as a dielectric layer with improved properties using spin coating.

“Pentacene thin-film transistor with poly (methymethacrylate-co-methacrylicacid) / TiO₂ nanocomposite gate insulator”, Thin Solid Films 518 (2009) 588–590

Poly (methymethacrylate-co-methacrylicacid) (PMMA-co-MAA) and TiO₂ has been dispersed in chloroform. Due to the strong interaction of TiO₂ particles with the carboxylic acid group (i.e. –COOH) of PMMA-co-MAA, the dispersion ability of composite has been increased. Nano particle TiO₂ can form heterosupramolecular assemblies in presence of π -conjugated materials containing carboxylic acid functional group. Due to this strong interaction, a homogeneous dispersion has been achieved without using surfactants. They have shown only 3 wt% solubility data.

Publication No. KR20020085255 (A))[Applicant: Donghoon Dgm Co Ltd [KR]] explains about coating solution which helps in smear fastness and absorptiveness and is improved in resolution and colour clearness. This patent is about regular printing of ink on paper and it has no relevance to our claims on an *ink of an electronic material (hybrid material)* used for manufacturing electronic devices such as capacitors and transistors.

Publication No. US20100006826 [Applicant: Weyerhaeuser Company, King County WA (US)] relates to use of high dielectric constant dielectric layer in dual layer dielectric organic thin film transistor. On top of first common organic layer, the use of second layer comprise of ferroelectric polymers, or silicon nitride or inorganic materials in the form of a precursor solution or suspended nanoparticles such as silicon dioxide, titanium dioxide, or aluminium oxide. In our invention, we present enhancement of dielectric constant of an organic dielectric (PVA) by adding nano-particles. Second,

Klaus et al. never talks about printing. But, here we claim inorganic-nanoparticle-incorporated-organic ink (hybrid-ink) which is inkjettable also.

Publication No. KR20080092686 (A) [Applicant: Samsung electro mech [KR]] relates metal nanoparticle, dispersed in non aqueous solvent, based ink. This study was to print conducting line. This is an ink using metallic nano-articles, but our claim is for an insulating ink containing oxide and organic dielectric material. This is totally different.

“Inkjet printing for flexible electronics: Materials, processes and equipments”, Chinese Science Bulletin, Volume 55, Number 30, 3383-3407.

Ping et al. explained the methodology of printing of inkjet, micro/nano-patterning technologies and electrohydrodynamic printing techniques. An overall review of printing is presented. Overview of commonly used ink is discussed in their paper. Concept of oxide nanoparticle incorporated organic dielectric ink as well as their printing is not mentioned anywhere in the paper.

“Polyethylenimine/N-Doped Titanium Dioxide Nanoparticle Based Inks for Ink-Jet Printing Applications” Journal of Applied Polymer Science, Vol. 122, 3630–3636 (2011).

Loffredo et al. reports, in the above mentioned journal paper, the dispersion behaviour of nitrogen doped TiO_2 (mixed phase- anatase and rutile) in ethyl alcohol while polyethylenimine (PEI) was used as a dispersing agent. But, after one day, slight settlement was noticed. With the remarkable property of N-doped TiO_2 , the possibility of dispersing these nanoparticles in solution might provide new inputs for the fabrication of scattering layers and in the photocatalytic and photovoltaic research sectors.

Again, it has no relevance to our claims on an *ink of an electronic material (hybrid material)* used for manufacturing electronic devices such as

capacitors and transistors. Use of TiO_2 dispersion is not new. In ceramic glaze industry, TiO_2 is used regularly. Similar thing is for paint industry also. Beside this, Titanium dioxide (TiO_2) nanoparticles are commonly employed in applications such as photocatalysts, photovoltaic cells, batteries, photochromic devices, electrochromic devices and gas sensors. But, we are claiming the process for a new application in printable electronics.

We used a rutile phase of TiO_2 , because of its higher dielectric constant compared to anatase. Incorporation with water soluble PVA is totally new approach, which could be very useful in the new era of printable electronics. Also, there was no report of incorporating TiO_2 nanoparticle in such high concentration in any solution. Our dispersion is stable for six month without any settlement. Also, no one has proposed to use this for increasing dielectric constant in printed dielectrics.

Thus, there are no reports on printing TiO_2 incorporating organic dielectric ink.

OBJECTS OF THE INVENTION:

An object of this invention is to propose a formulation of an organic ink;

Another object of this invention is to propose a method for preparing a formulation of an organic ink;

Still another object of this invention is to propose ink which is water based;

Further, object of this invention is to propose a composite ink used for printing;

Still further object of this invention is to propose a nano composite ink formulation containing TiO_2 nano particles and polyvinyl alcohol well dispersed in DI water.

BRIEF DESCRIPTION OF THE INVENTION:

According to this invention there is provided a hybrid ink formulation comprising: PVA and TiO_2 in a ratio of 10:1 in DI water.

In accordance with this invention there is also provided a method of making a hybrid ink formulation comprising:
dissolving TiO_2 solution in DI water separately,
dissolving PVA is also in DI water,
mixing the individual solution at room temperature.

BRIEF DESCRIPTION OF THE ACCOMPANY DRAWING:

Fig 1: Photograph of TiO_2 incorporated PVA solution which was made of Approach 1,2,3 & 4.

DETAILED DESCRIPTION OF THE INVENTION:

This invention relates to a homogeneous dispersion of inorganic nano particles and organic dielectric material.

(A) Homogeneous dispersion: To formulate TiO_2 incorporated PVA solution, four different approaches were adopted which are given below.

Approach 1: Pouring both PVA and TiO_2 in DI water, followed by stirring up to 24 hours at two different temperatures, room temperature and 70°C .

Approach 2: Dissolving PVA in DI water first by stirring at 70°C for 12 hours, then addition of TiO_2 in crystal clear PVA solution, followed by stirring up to 24 hours at two different temperatures, room temperature and 70°C .

Approach 3: Dissolving TiO_2 in DI water first, then addition of PVA in crystal clear

TiO_2 solution, followed by stirring up to 24 hours at two different temperatures, room temperature and 70°C .

Approach 4: Dissolving TiO_2 solution first in DI water, separately PVA was dissolved in DI water with stirring for 12 hours at 70°C . Finally, mixing of individual solution together is at room temperature.

Approach 4 is the successful procedure and is non-obvious. Crystal clear solution was not achieved in case of approach 1, 2 & 3. But in approach 4, we got transparent solution.

The problem comes because we cannot take TiO_2 at higher temperature and PVA does not dissolve at room temperature. So our idea is to dissolve PVA and TiO_2 separately and mix at room temperature. By this technique, TiO_2 can be incorporated $>50\text{wt}\%$ in PVA- TiO_2 system, which is significant compared to previously reported system.

To dissolve PVA in DI, optimized parameters are baking temperature 70°C and stirring time 12 hours.

(B) Homogeneous dispersion to ink:

Next, to print this homogeneous dispersion, surface tension and viscosity is specified, depending on the technique being used.

Surface tension of PVA solution as well as TiO_2 solution was measured individually, which is given in Table 1. It can be seen that surface tension is mainly determined by solvent not solute concentration. Surface tension of DI water was slightly decreased by mixing PVA powder and slightly increased by incorporating TiO_2 nanoparticles.

Table 1: Surface tension and viscosity of different solution (at 25°C)

Sr No	Composition	Surface tension (25°C) (dyne/cm)	Viscosity (cP)
1	2.5wt% PVA in DI water	64.15	4.01
2	1.25wt% PVA in DI water	70.47	2.19
3	0.125 wt% TiO_2 in DI water	82.18	1.01
4	D.I. water	71.97	1.00
5	1.25wt% PVA + 0.125wt% TiO_2 in DI water	72.9	2.19
6	1.25wt% PVA + 0.625wt% TiO_2 in DI water	74	2.7

Effect of surfactant on surface tension was measured (Table 2). Significant drop in surface tension was noticed when surfactant was added. TritonX-100 was used as a surfactant for all inks.

Table 2: Effect of surfactant on viscosity and surface tension (at 25°C)

Sr No	Composition	Vol % TritonX- 100	Surface tension (dyne/cm)	Viscosity (cP)
1	1.25wt%PVA in DI water	0	70.47	2.19
2	1.25wt%PVA in DI water	0.1	27.7	2.18
3	1.25wt% PVA + 0.125wt%TiO ₂ in DI water	0	72.9	2.19
4	1.25wt% PVA + 0.125wt%TiO ₂ in DI water	0.1	28.07	2.18

(C) Inkjet printing

We have fabricated capacitors using these inks in an inkjet printer.

(D) Improvement of dielectric constant with TiO₂ nanoparticle incorporation in PVA

PVA (wt%)	TiO ₂ (wt% of PVA)	Technique	Thickness (nm)	Capacitance nF/cm ²	Dielectric constant
5	0	Spin coat	510	13.05	7.4
1.25	0	Spin coat	63	107.81	7.7
1.25	10	Spin coat	78	115.29	10.2
1.25	50	Spin coat	149	106.25	17.9

Literature value of dielectric constant of PVA is in between 3.5-10. Viscosity & surface tension of 50wt% TiO₂ in PVA are 2.78 cP and 29.6 dyne/cm.

EXAMPLES:

PVA was selected as a dielectric material for printing, because of its low cost, easy accessibility, better capacitor performance and relatively high dielectric constant compared to other organic dielectric. Its dielectric constant (ϵ) is around 3.5-10. PVA solution in water is not readily printable because of its high viscosity and surface tension. We have formulated PVA ink and have printed capacitors using inkjet printing on PET substrate using the same.

Concept of incorporating TiO_2 in PVA is implemented to enhance the dielectric constant of PVA

We have invented a process to incorporate >50 wt% TiO_2 nano-particles in PVA ink. The same has also been used for Inkjet printing of TiO_2 nanoparticle incorporated PVA layer.