**Serial No.**: <u>09/672,791</u>

Filing Date: 29 SEPTEMBER 2000

Inventor: <u>RANGANATHAN SHASHIDHAR</u>

#### **NOTICE**

The above identified patent application is available for licensing. Requests for information should be addressed to:

> ASSOCIATE COUNSEL (PATENTS) CODE 1008.2 NAVAL RESEARCH LABORATORY WASHINGTON DC 20375

DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited PATENT APPLICATION/TECHNICAL DIGEST PUBLICATION RELEASE REQUEST

FROM: Associate Counsel (Patents) (1008.2)
TO: Associate Counsel (Patents) (1008.2)

- Via: (1) Ranganthan Shashidhar (Code 6900)
  - (2) Division Superintendent (Code 6900
  - (3) Head, Classification Management & Control (Code 1221)

**SUBJ:** Patent Application/Technical Digest entitled: **"ELECTRONIC DISPLAY DEVICE AND COATINGS THEREOF"** Request for release for publication.

**REF:** (a) NRL Instruction 5510.40C (b) Chapter 6, ONRINST 5870.1C

ENCL: (1) Copy of Patent Application/Technical Digest

1. In accordance with the provision of references (a) and (b), it is hereby requested that the subject Patent Application/Technical Digest be released for publication.

2. It is intended to offer this Patent Application/Technical Digest to the National Technical Information Service, for publication.

3. This request is in connection with Navy Case No, 82,573

IOHN J. -KARASEK Associate Counsel (Patents)

FIRST ENDORSEMENT

Date:

**FROM:** Ranganathan Shashidhar (Code 6900) **TO:** Division Superintendent (Code 6900)

1. It is the opinion of the Inventor(s) that the subject Patent Application/Technical Digest (is) (is not) classified and there is no objection to public release.

Rist

Inventor's Signature

NDW-NRL 551/3001 (Rev. 6-89) (Page 1 of 2)

#### SECOND ENDORSEMENT

Date:

FROM: Division Superintendent (Code 6900)
TO: Classification Management & Control (Code 1221)

1. Release of Patent Application/Technical Digest (is) (is not) approved.

2. To the best knowledge of this Division, the subject matter of this Patent Application/Technical Digest (has) (has not) been classified.

3. This recommendation takes into account military security, sponsor requirements and other administration considerations and there in no objection to public release.

i 🛛 sion Superintendent

THIRD ENDORSEMENT

Date:

**FROM:** Head, Classification & Control (Code 1221) **TO:** Associate Counsel (Patents) (1008.2)

1. This Patent Application/Technical Digest is authorized for public release.

Martin alluno

Head, Classification, Management & Control

NDW-NRL 5511/3001 (Rev. 6-89) (Page 2 of 2)

Patent

Inventors: Shashidhar et al Application Serial Number:

Navy Case Number: 82,573

DIIC QUALITY INSTREET

20010102 024

#### **Electronic Display Device And Coatings Therefor**

Background of the Invention

Field of the Invention:

This invention pertains to the field of electronic display-related devices, such as liquid crystal displays and organic light emitting displays, and to highly transparent and electrically conducting processable coating compositions containing a polymer.

Description of Related Art:

Most of the current liquid crystal displays use glass coated with indium tin oxide as the conducting substrates. These conducting substrates serve as electrodes to apply a voltage to the liquid crystal. Fabrication of indium tin oxide coating on glass is carried out at an elevated temperature of about 250°C in order to have acceptably short deposition times. This has been problematic for incorporating other components, like color filters, into the display devices. More importantly, the fact that indium tin oxide deposition is a high temperature process makes it unsuitable for plastic displays. This is because plastics do not stand temperatures greater than about 150°C. Also, indium tin oxide (ITO) deposition is not a web-compatible process and hence not suitable for large scale manufacturing of plastic liquid crystal displays.

20

5

10

15

Although electronically conducting polymers have been known since 1973, the possibility of using conducting polymer coated plastic for liquid crystal displays was not considered until recently. This was essentially because none of the available conducting polymers, like polyaniline, polypyrrole or polythiophene, showed the necessary combination of

1

DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited

5

10

15

20

Patent

Navy Case Number: 82,573

properties suitable for liquid crystal displays. Recently, it was demonstrated that thin polypyrrole films, processed using an in-situ deposition process, have surface resistance and optical transparency, the two important parameters that are most relevant to liquid crystal displays, that are reasonably adequate for liquid crystal displays. However, two major problems still remained that needed to be solved before conducting polymers could be seriously considered for liquid crystal displays and other display applications. The first problem concerns the competition between the surface resistance and optical transparency. For liquid crystal displays, as well as for other display-related applications, the surface resistance has to be as low as possible whereas the optical transparency has to be as high as possible. All attempts to optimize these two properties essentially gave the same trends for any variation associated with a processing parameter - a reduction in the surface resistance was always accompanied by a concomitant reduction of the optical transparency. In other words, reduction of surface resistance always led to a serious compromise on the optical transparency.

The second problem, which has also been common to all conducting polymers mentioned above, has been the difficulty in processing. For instance, polypyrrole is not soluble in most of the solvents and hence is not a processable conducting polymer. Attempts have been made to improve solubility by attaching surfactant groups or alkyl chains chemically to the pyrrole structure. However, such attachments also led to a drastic reduction in conductivity and increase in surface resistance. Thus, conducting polymers that can be easily processed and whose films have low surface resistance and high optical transparency, have remained elusive.

Patent

Inventors: Shashidhar et al Application Serial Number:

Navy Case Number: 82,573

5

20

#### Objects and Brief Summary of the Invention

An object of the invention is an electronic display-related device characterized by a transparent and conducting processable film.

Another object of the invention is a coating on a substrate that is fabricated at a temperature that is suitable for plastic displays.

10 Another object of this invention is a polymer coating for electronic display devices that is modestly priced relative to the prior art coating compositions for similar purposes.

Another object of this invention is an optically transparent and electrically conducting polymer coating composition for electronic display devices wherein surface resistance is substantially independent of optical transparency.

# 15 These and other objects of this invention are achieved by an electronic display device that is characterized by an optically transparent and electrically conducting thin polymer

processable film coating composition disposed on a substrate that can be fabricated at

temperatures that are not degrading to plastics.

#### Brief Description of the Drawings

Fig. 1 is a schematic illustration of an electronic liquid crystal display device showing the polymer coating composition disposed on a substrate.

Fig. 2 is a schematic illustration of an electronic light emitting display device showing the polymer coating disposed on a substrate.

Fig. 3 is a graph of optical transmittance and surface resistance plotted against

5

10

20

Patent

Navy Case Number: 82,573

sulfosalcilylic acid concentration of a polymer composition spin-coated on a plastic substrate at 500 rpm.

Fig. 4 is a graph of optical transmittance and surface resistance plotted against the typical coating composition components, including glycerol, with the coating composition spin-coated on a plastic substrate at 500 rpm.

Fig. 5 is a graph showing variation of optical transmittance and surface resistance with coating compositions containing sulfosalicylic acid (SSA); glycerol; mixtures of sulfosalicylic acid and glycerol; and mixtures of glycerol, sulfosalicylic acid, and sodium salt of anthraquinone-2-sulfonic acid (AQSA).

Fig. 6 is a graph showing the positive effect of a dopant or a mixture thereof on surface resistance and optical transmittance of a composition spin-coated on a plastic substrate at 1000 rpm.

#### Detailed Description of the Invention

This invention pertains to an electronic display device and to a coating composition therefor. The electronic display device is characterized by an optically transparent and electrically conducting processable coating composition disposed on a substrate. The coating composition includes a processable and dispersible polymer, a dispersant for the polymer, a nonionic polyhydroxy compound, and an ionic dopant. The coating composition is processable in that it is soluble and/or dispersible, has high optical transparency above 70% and low surface resistance of less than about 700  $\Omega/\Box$ .

5

10

15

20

#### Patent

#### Navy Case Number: 82,573

Figs. 1 and 2 schematically illustrate typical electronic display devices. Fig. 1 shows a liquid crystal display device which modulates light upon application of voltage, and Fig. 2 shows a light emitting display device which produces light on application of voltage. Other electronic display devices are also contemplated herein characterized by the optically transparent and electrically conducting processable coating compositions disposed on a suitable substrate.

The Fig. 1 sketch shows principal components of typical electronic liquid crystal display device which modulates light directed thereat on application of voltage. The device 100 of Fig. 1 includes a pair of spaced optically transparent substrates 102, 104 with substrate 102 being the lower and substrate 104 being the upper substrate. The substrates are typically planar although curved configurations can be used. Material of the substrates is optically transparent and is typically glass but it can be anything else such as plastic, metal, ceramic, and the like, provided it can withstand fabrication temperature without disintegrating in any substantial respect. Disposed on the lower transparent substrate 102 is the optically transparent and electrically conducting processable coating film 106 which is more fully defined below. Similar or identical is the upper film 108 which is disposed on the upper transparent substrate 104. Films 106 and 108 are typically thin, varying in thickness from about 5 nm to about 5 µm, although the thickness can be anything desired. Thin films are preferred. Disposed on lower coating 106 is the lower aligning surface 110 and a similar or another upper aligning or even non-aligning surface 112 is disposed against the upper coating 108. Between the two surfaces is disposed

Patent

Navy Case Number: 82,573

5 liquid crystal material 114.

> The schematic of the liquid crystal display device 100 shown in Fig. 1 is in the form of a stack and modulates light 116 directed at the stack from below on application of voltage between the transparent and conduction coatings 106, 108, as shown generally by the circuit designated 118.

10 Fig. 2 is a schematic illustration of another electronic display device, in this case a light emitting display device 200. The electronic display device of Fig. 2 includes a pair of spaced substrates, i.e., lower substrate 202 and upper substrate 204. Again, the substrates can be of any material desired, although they are typically of glass or plastic. If plastic substrates are used, care must be taken not to expose them to high temperatures at which they may degrade. Adjacent to 15 and in contact with and between the substrates are lower transparent conducing coating 206 and the upper like coating 208. These coatings 206, 208 are similar or identical to the coatings 106, 108 in the device a Fig. 1. Between the transparent and conducing processable coatings 206, 208 are anode 210 disposed a adjacent and in contact with the lower coating 206 and cathode 212, spaced above the anode, disposed adjacent and in contact with the upper coating 208. Between the anode and the cathode is the light emitting diode material 214.

20

The schematic of the electronic light emitting display device 200 shown in Fig. 2 is in the form of a stack and produces light on application of voltage between the transparent and conducting coatings 206, 208.

The coatings or coating compositions or thin films or layers 106, 108 in the

Patent

Navy Case Number: 82,573

representation of electronic liquid crystal display device of Fig. 1 and coatings 206, 208 in the electronic light emitting display device of Fig. 2 are optically transparent, electrically conducting, and processable. The coatings have optical transmission to visible light having wavelength of about 400-700 nm of greater than about 70%, preferable excess of about 80%. Surface resistance of the coatings is less than about 700 Ω/□, preferably less than about 500
Ω/□. The polymer in the coating is soluble or dispersible in water or another solvent that might be used. By adding the additives to the polymer, surface conductivity of the coating has been enhanced approximately 10 fold, from about 6500 Ω/□ to below about 800 Ω/□.

The coating composition includes the following components before removal of the solvent:

1. electrically conducting, processable polymer	broad range 0.1-5	narrow range 0.2-2
2. dispersant for the polymer	0.1-5	0. 2-2
3. polyhydroxy compound	0.1-20	0.2-10
4. ionic dopant	0.1-20	0.2-10
5. solvent	remainde	r to 100 %

20

25

15

The polyhydroxy compound has the formula  $CH_2$ . OH-(-CH OH-)<sub>n</sub>-CH<sub>2</sub>OH and  $(CH_2OH)_nO$  (CH<sub>2</sub>OH)<sub>n</sub> where n is up to 20, preferably, 1-10. In a particularly preferred embodiment, the components in weight percent are as follows: amount of the polymer is 0.2-1%, such as about 0.5%; amount of the dispersant is 0.2-1%, such as about 0.8%; amount of the polyhydroxy compound is 1-10%, such as about 5%; and amount of the dopant is 1-10%,

5

10

15

20

Patent

Navy Case Number: 82,573

such as about 5 %. There appears to be no chemical reaction between components of the composition and the ratio of the components remains the same before or after removal of the solvent.

In absence of solvent, i.e., on dry basis, the broad and narrow ranges of the components is as follows:

	broad range	narrow range	
1. electrically conducting, processable polymer	0.2-95	1-75	
2. dispersant for the polymer	0.2-95	1-75	
3. polyhydroxy compound	0.3-99	1-95	
4. ionic dopant	0.3-99	1-95	

The solvent, particularly water, is an indispensible coating component since the coating composition must be film-forming and processable. If not enough or too much solvent is used, the resulting coating composition will not be film-forming and/or processable and the composition will not be suitable for purposes herein. The polymer and the dispersant are typically used in the form of an aqueous solution; the polyhydroxy compound is typically dissolved in a lower alkyl alcohol and then mixed into the aqueous solution; and the dopant is typically dissolved in water and then mixed into the aqueous solution, which is the final solution tha is coated on the substrate.

The polymers contemplated herein are electrically conducting polymers such as polyanilines, polypyrroles, polythiophenes, polyphenylenes, and poly(p-phenylene vinylene).

5

10

15

20

#### Patent

Navy Case Number: 82,573

The polyaniline family is attractive for its ability to form processable conductive forms at relatively low cost in bulk amounts. Unfortunately, due to the presence of benzidine moieties in the polymer backbone, which might yield toxic (carcinogenic) products upon degradation, interest in polyaniline chemistry has been limited. The preferred polymer for purposes herein is selected from polyethylene dioxythiophene containing the following repeating unit:



where  $R^1$  and  $R^2$  are selected from phenyl and alkyl groups containing 1-15 carbon atoms. Since processability is an important facet of the polymer and since processability is reduced by elongating the chain(s) on the molecule and including some substituents, in a preferred embodiment, a suitable polymer is a polyloweralkylene dithiophene where  $R^1$  and  $R^2$ that are selected from hydrogen, methyl and ethyl moieties. The most preferred polymer is poly (3,4, ethylene- dioxythiophene) where  $R^1$  and  $R^2$  are hydrogen molecules, whose weight average molecular weight is in the range of 10,000 to 150,000.

Any suitable dispersant can be used to either solubilize or to disperse the polymer in water or another suitable solvent. For polyethylene dioxythiophene polymer, polystyrene sulfonic acid dispersant is suitable. Weight average molecular weight of a polymeric dispersant,

#### Patent

#### Navy Case Number: 82,573

if it is a polymer, is such that it forms a solution with the polymer in water. Weight average molecular weight of the polystyrene sulfonic acid is estimated to be in the range of 100,000 to 200,000.

The polyhydroxy compound appears to improve long-range order of conducting molecules of the polymer and reduces defects between polymer domains. Suitable polyhydroxy compounds are linear and have the general structure  $CH_2$ . OH-(-CH OH-)  $_n$ -CH  $_2$ OH and  $(CH_2OH)_nO(CH_2OH)_n$  where n is up to about 20, typically 1-10. Certain surfactants were tried but the resulting films were unstable in that the films were too soluble in water. For instance, glucose, fructose and galactose also produced films that were too soluble in water. Particularly suitable herein are the polyhydroxy compounds containing at least two hydroxyl (OH) groups and include sorbitol, glycerol, diethylene glycol, propylene glycol, and the like.

15

20

10

5

The fourth component in the composition is an ionic organic dopant which further improves electrical conductivity of the composition but which appears to reduce its transparency somewhat. So, a suitable ionic dopant is any component that is compatible with components of the composition, improves its conductivity and which is not unduly deleterious with respect to light transmission when the composition is applied onto the substrate. Specific examples of suitable herein dopants include sulfosalicylic acid, sodium salt of anthraquinome-2 sulfonic acid and m-cresol. Other suitable ionic and organic dopants can also be used.

It appears that the polyhydroxy compoun and ionic the dopant components of the coating composition act synergistically with respect to electrical conductivity and optical transparency of

#### Patent

Navy Case Number: 82,573

5 the composition. Furthermore, there does not appear to be any chemical reaction taking place, as it relates to formation of compounds, when the composition components are combined.

The fifth component in the coating composition is a solvent which makes it possible to make a film of the composition and enable preparation of a processable coating composition. Typically, the solvent is water.

Preparation of the coating composition involves combining a number of solutions which contain the composition components. The first solution is typically an aqueous solution of the polymer and the dispersant; the second solution is typically an aqueous solution of the polyhydroxy compound; and the third solution is typically an aqueous solution of the ionic dopant. Typically, the coating composition is prepared by mixing the three solutions at room temperature and then applying them to a substrate, followed by annealing to remove the solvent and to treat the coating composition at a suitable temperature and for a sufficient duration that does not damage the substrate. Annealing or heating the composition results in molecular alignment self organization and concomitant improved electrical conductivity and physical integrity. If water is the solvent, annealing is typically carried out at 120-125 °C for 4-5 minutes.

Having described the invention, the following examples are given as particular embodiments thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or claims in any manner.

Patent

Inventors: Shashidhar et al Application Serial Number:

Navy Case Number: 82,573

#### 5

10

15

20

Examples

Commercial Batron P polyethylene dioxythiophene aqueous solution is available from the German company Bayer AG. The Batron P is an aqueous solution composed of 0.5 % by weight poly(3,4 - ethylenedioxythiophene) polymer and 0.8% by weight polystyrene sulfonic acid dispersant. A second solution was prepared by dissolving 0.8g D-sorbitol polyhydroxy compound and 0.6 g glycerol polyhydroxy compound in 1ml methanol. A third solution was prepared by gradually dissolving at 70-80°C 0.05g of sodium salt of anthraquinone -2- sulfonic acid ionic dopant and 0.1g of sufosalicylic acid ionic dopant in 2ml of deionized water. The coating composition solution was prepared by pouring into a 100-ml. glass flask 10 ml of the Batron P aqueous solution containing the polymer and the dispersant, 1 ml of the second alcohol solution containing the polyhydroxy compounds and the third aqueous solution containing the ionic dopants. The flask contents on weight percent were as follows:

polymer	0.53
dispersant	0.82
polyhydroxy compound	0.5-20
ionic dopant	0.5-8
water	to 100 %

Cleaned solid substrates were used, the substrates being poleythylene terephthalate (PTE) measuring about 2.2 cm on a side with a thickness of about 250  $\mu$ m.

The conductivity measurements were performed at different times of 0, 1, 2 and 24

Patent

Inventors: Shashidhar et al Application Serial Number:

Navy Case Number: 82,573

5 hours.

10

15

20

Surface resistance (conductivity) was measured using Signatone Four-Point Probe Resistivity Mapping System(SYS-301) connected to Keithley 224 Programmable Current Source and Keithley 196 System Digital Multimeter. Film transparency was measured for every substrate by using Gary 5 UV-vis Spectro-meter at transmittance mode. The film thickness was determined by using Profilometer. The accuracy of film thickness was also confirmed by Scanning Electron Microscope.

#### Example 1

The PTE plastic substrates were used as received, i.e., without any surface treatment or cleaning, gave water contact angle of 45°. The above coating composition was spin- coated on the substrates and annealed at 120-125°C for 4-5 minutes with the following results:

Spin Rate ( <u>rpm)</u> 500	Surface Resistance $\frac{R_s(\Omega/\Box)}{no \text{ film}}$	Optical transmittance (T%) no film
1000	1500	90
2000	2300	95

No film was formed at 500 rpm probably due to the fact that the substrate surfaces were not cleaned and because of the low speed. The film formed at 1000 rpm and at 2000 rpm was not uniform in that some areas on the substrates were left uncoated.

#### Example 2

25

The plastic substrates, cleaned by soaking for 15 minutes under sonication (Method I)

5

10

15

#### Patent

Navy Case Number: 82,573

gave water contact angle of 40°. A mixture of 10 ml of the Batron P aqueous solution and 0.5g glycerol dissolved in 1ml deionized water was spin coated on the cleaned substrates and annealed at 120-125°C for 4-5 minutes with the following results.

Spin Rate <u>(rpm)</u> 500	Surface Resistance <u>R<sub>s</sub> (Ω/□)</u> 950	Optical transmittance (T%) 85
1000	1300	90
2000	2200	95

#### Example 3

The plastic substrates, cleaned by dipping into 10% HCl solution for 10 minutes under sonication then were sequentially rinsed with deionized water, methanol, and acetone (Method II) gave water contact angle of 35°. A mixture of 10 ml of the Batron P aqueous solution and 0.5g glycerol dissolved in 1ml of deionized water was spin coated on the cleaned substrates and annealed at 120-125°C for 4-5 minutes with the following results:

20	Spin Rate <u>(rpm)</u> 500	Surface Resistance $\frac{R_s(\Omega/\Box)}{880}$	Optical transmittance (T%) 84
	1000	1300	87
	2000	2200	92
25		Example 4	

The plastic substrates, cleaned by being kept in 10% KOH in isopropanol for 20 minutes

5

15

Patent

Navy Case Number: 82,573

then washed sequentially with acetone and methonol (Method III), gave water contact angle of 25°. A mixture of 10 ml of the Batron P aqueous solution and 0.5g glycerol dissolved in 1ml of deionized water was spin coated on the cleaned substrates and annealed at 120-125°C for 4-5 minutes with the following results:

10	Spin Rate <u>(rpm)</u> 500	Surface Resistance $\frac{R_s(\Omega/\Box)}{880}$	Optical transmittance (T%) 84
	1000	1300	87
	2000	2200	92
		Example 5	

Example 5

The plastic substrates, cleaned by first treating with plasma stream inside a plasma generator for ½ hour and then by rinsing sequentially with methanol and acetone (Method IV) gave water contact angle of about 3°. A mixture of 10 ml of the Batron P aqueous solution and 0.5g glycerol dissolved in 1ml of deionized water was spin coated on the cleaned substrates and annealed at 120-125°C for 4-5 minutes with the following results:

20	Spin Rate ( <u>(rpm)</u> 500	Surface Resistance <u>R<sub>s</sub> (Ω/□)</u> 790	Optical transmittance (T%) 86
	1000	1300	90
	2000	2000	
25		Example 6	

Only the Batron P solution was spin coated on plastic substrates cleaned by keeping the

Patent

Navy Case Number: 82,573

5 substrates in 10% KOH in isopropanol solution for 20 minutes and then washed sequentially in acetone and methanol (Method III ). After annealing as previously, the following results were

obtained:

10

15

20

25

Spin Rate (rpm) 500	Surface Resistance <u>R<sub>s</sub> (Ω/□)</u> 2800	Optical transmittance (T%) 86
1000	3600	89
2000	5800	94

It should be apparent from the above results that although transmittance is good, surface resistance of the film is too high.

#### Example 7

Mixtures of 10 ml of the Batron P solution mixed with different amounts of sulfosalicylic acid (SSA) dopant were prepared according to the general procedure, but in absence of glycerol, and then spin-coated on PET plastic substrates pre-cleaned by Method III. The SSA dopant amounts were 0.05g, 0.1g, 0.2g, 0.4g, 0.6g, and 0.8g. After heating or annealing the coated substrate as previously, the following results were obtained:

SSA Amount (g)	Spin Rate (rpm)	Surface Resistance <u>R₅(Ω/□)</u>	Optical Transmittance (T%)
0.05	500	1100	78
0.05	1000	1700	87
0.05	2000	2800	92
0.1	500	700	74

#### Patent

#### Navy Case Number: 82,573

0.1	1000	1300	83
0.1	2000	2300	91
0.2	500	330	64
0.2	1000	750	79
0.2	2000	1500	88
0.4	500	150	44
0.4	1000	500	77
0.4	2000	850	82
0.6	500	100	28
0.6	1000	350	66
0.6	2000	850	80
0.8	500	100	19
0.8	1000	350	60
0.8	2000	780	80

20

25

15

5

10

The above results show a reduction in surface resistance and a concomitant reduction in light transmittance. This trend is clearly represented in Fig. 3. Although at 0.2g SSA the surface resistance is an acceptable 330  $\Omega/\Box$ , transmittance is an unacceptable 64%.

#### Example 8

Five mixtures of the coating composition were prepared by mixing 10 ml of the Batron P aqueous solution with different amounts of glycerol and then spin coated on plastic substrates cleaned by Method III and annealed as previously. Test results are given below:

Glycerol Amount	Spin Rate	Surface Resistance	Optical Transmittance
<u>(g)</u>	<u>(rpm)</u>	$\underline{\mathbf{R}}_{s}(\underline{\Omega}/\Box)$	<u>(T%)</u>

#### Patent

## Navy Case Number: 82,573

-

•				
5	0.05	500	880	69
	0.05	1000	1100	80
	0.05	2000	2000	88
	0.1	500	600	70
	0.1	1000	1000	80
10	0.1	2000	1600	88
	0.2	500	450	69
	0.2	1000	850	81
	0.2	2000	1400	88
	0.4	500	380	61
15	0.4	1000	650	79
	0.4	2000	1100	87
	0.6	500	350	68
	0.6	1000	630	81
	0.6	2000	1000	87
20	0.8	500	330	72
	0.8	1000	580	82
	0.8	2000	880	89
	1	500	330	72
	1	1000	580	82
25	1	2000	880	89
	1.5	500	350	72
	1.5	1000	600	82
	1.5	2000	920	91

5

10

25

#### Patent

#### Navy Case Number: 82,573

2	500	400	74
2	1000	600	82
2	2000	950	91

The above data shows dramatic results which are also self-evident in Fig. 4. Unlike the coating consisting of the polymer, dispersant and the ionic dopant, surface resistance and transmittance are now decoupled, meaning that a variation in one is not accompanied by a variation in the other. Results in the above table, represent a demonstration of the ability to vary surface resistance without varying optical transmission.

#### Example 9

In order to see the effect of adding the ionic dopant sulfosalicylic acid (SSA) and the nonionic polyhydroxy compound glycerol, mixtures of the Batron P solutions, the SSA solutions and glycerol solutions were prepared varying the amount of glycerol. 10 ml of the Batron P solution was used. The SSA solution was 0.1g SSA dissolved in 1ml of methanol. The glycerol solutions contained varying amounts of glycerol dissolved in 1ml of deionized water. The amounts of glycerol varied from 0.5g to 2g. Annealing or drying were conducted as before. Results are set forth below:

Glycerol Amount	Spin Rate (rpm)	Surface Resistance $\underline{R}_{s}(\Omega/\Box)$	Optical Transmittance (T%)
0.05	500	560	70
0.05	1000	1000	82
0.05	2000	1900	88

### Patent

# Navy Case Number: 82,573

:

	<b></b>			
5	0.1	500	390	72
	0.1	1000	750	82
	0.1	2000	1200	88
	0.2	500	350	74
	0.2	1000	700	82
10	0.2	2000	1100	90
	0.4	500	300	74
	0.4	1000	500	81
	0.4	2000	900	88
	0.6	500	290	72
15	0.6	1000	480	81
	0.6	2000	750	87
	0.8	500	250	74
	0.8	1000	390	81
	0.8	2000	650	87
20	1	500	350	74
	1	1000	520	82
	1	2000	800	87
	1.5	500	390	74
	1.5	1000	580	82
25	1.5	2000	900	88
	2	500	520	75
	2	1000	620	83
	2	2000	930	88

.....

20

25

.

5

10

20

25

#### Patent

Navy Case Number: 82,573

Again, the decoupling of the surface resistance and transmittance variations with glycerol concentration variation is seen for all speeds. An outstanding coating composition appears to be one prepared by mixing 10 ml Batron P aqueous solution, 1 ml methanol containing dissolved therein 0.1g sulfosalicylic acid, and 1 ml deionized water containing dissolved therein 1.6g glycerol. The composition is spin-coated on a plastic substrate at 1000 rpm and annealed or heated at 120 ° C for 2 minutes. The surface resistance for this coating was 480  $\Omega/\Box$  and its optical transmittance was 81 %.

#### Example 10

The coating compositions here were mixtures of 10 ml Batrol P solution, 1 ml 15 methanol containing 0.05g of sodium salt anthraquinone -2- sulfonic acid ionic dopant dissolved therein and 1 ml methanol containing 0.1g sulfosalicylic acid ionic dopant dissolved therein and different amounts of glycerol varying from 0.05g to 1.5 g. Annealing was conducted as before. Results are given below:

Glycerol Amount	Spin Rate <u>(rpm)</u>	Surface Resistance $\underline{R}_{s}(\Omega/\Box)$	Optical Transmittance (T%)
0.05	500	400	66
0.05	1000	880	80
0.05	2000	1600	87
0.1	500	250	64
.01	1000	600	80
0.1	2000	950	84
0.2	500	230	65

5

10

15

20

25

#### Patent

#### Navy Case Number: 82,573

		-	
0.2	1000	550	77
0.2	2000	900	84
0.4	500	200	65
0.4	1000	450	78
0.4	2000	750	85
0.6	500	180	65
0.6	1000	380	77
0.6	2000	660	84
0.8	500	190	65
0.8	1000	380	78
0.8	2000	720	84
1	500	220	64
1	1000	500	78
1	2000	800	84
1.5	500	280	65
1.5	1000	600	78
1.5	2000	980	85

#### Example 11

In this example, comparison was made of surface resistance and transmittance values for glycerol and mixtures of glycerol and different dopants for coating compositions spin-coated at 1000 rpm on PET plastic substrates. The first coating composition was a mixtire of 10 ml Batron P aqueous solution and 1 ml methanol having dissolved therein 0.1 g sulfosalicylic acid (SSA). The second one was a mixture of 10 ml Batron P solution and 1 ml methanol having dissolved

5

10

15

20

25

Patent

Navy Case Number: 82,573

therein 0.6 g glycerol. The third one was a mixture of 10 ml Batron P solution and 1 ml methanol having dissolved therein 0.1 sulfocalicylic acid and 0.6 g glycerol. The fourth one was a mixture of 10 ml of Barton P first solution and a second solution of 1 ml methanol and 1 ml water having dissolved therein 0.1 g sulfosalicylic acid, 0.6 g glycerol and 0.05 g sodium salt of anthraquinone-2-sulfonic acid (AQSA).Water was needed to solubilize AQSA. Annealing was conducted as before. The data is represented in the graph of Fig. 6 which shows a large variation of surface resistance from 1400  $\Omega/\Box$  to 400  $\Omega/\Box$  while light transmission remains more or less constant at about 80 %.

#### Example 12

This example demonstrates decoupling of surface resistance and transmittance. Here, 10 ml of Batron P solutions were mixed with varying amounts of D-sorbitol. The sorbitol was dissolved in 1 ml of deionized water. Amount of sorbitol varied from 0.2 to 0.8 g. Annealing was conducted as before. Test data is given below:

	Sorbitol Amount (g)	Spin Rate (rpm)	Surface Resistance $\frac{R_s(\Omega/\Box)}{\Delta}$	Optical Transmittance (T%)
	0.2	500	620	61
•	0.2	1000	1300	80
	0.2	2000	2000	86
	0.4	500	500	67
	0.4	1000	1100	82
	.04	2000	1600	87

#### Patent

#### Navy Case Number: 82,573

0.8	500	400	62
0.8	1000	700	81 .
0.8	2000	1100	87
1.2	500	450	65
1.2	1000	720	81
1.2	2000	1100	88
1.6	500	550	67
1.6	1000	1000	80
1.6	2000	2000	87

10

5

15

20

The above data demonstrates the decoupling effect of surface resistance and light transmission whether glycerol or sorbitol are used.

Thus was demonstrated the new concept that surface resistance of a conducting polymer film can be tuned without compromising the optical transmission by adding a non-ionic sugarlike carbohydrate addition and an ionic dopant.

While presently preferred embodiments have been shown of the novel electronic display devices and the coating composition therefor, and of the several modifications discussed, persons skilled in this art will readily appreciate that various additional changes and modifications may be made without departing from the spirit of the invention as defined and differentiated by the following claims.

Patent

Navy Case Number: 82,573

#### Abstract

A coating composition and an electronic display device characterized by having the composition disposed on a pair of spaced substrates. The composition is processable, has surface resistance of about 700  $\Omega/\Box$  or less and optical transmittance of about 70% or higher. The composition is a dilute solution comprising the following components given in weight percent:

electrically conducting polymer0.1-5dispersant for said polymer0.1-5polyhydroxy compound0.1-20ionic dopant0.1-20solventto 100 %

15

10



Figure 1

# Figure 2

# LED (200)





Glass / plastic

Conductive layer

LED Material Cathode Conductive layer

Glass / plastic





Page 1

Chart<sup>1</sup>



Figure 4 : Dependance of the surface resistance and optical transperency on glycerol

-Chart4-

Page 1



Figure 5 : Effect of glycerol concentration on SSA (0.1g) and AQSA-(0.05g) doped films at speed 500 rpm.

Page 1





Chart19

-Page 1....