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(54) Title: LIQUID PRECURSOR FOR CHEMICAL VAPOR DEPOSITION

(57) Abstract

Composition containing a chlorinated organotin derivative and a polyfluoroalkyl compound and/or a halo polyfluoroalkyl compound useful for CVD formation of fluorine doped tin oxide coatings.

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LIQUID PRECURSOR FOR CHEMICAL VAPOR DEPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to new liquid coating compositions useful for the production of improved fluorine-doped tin oxide layers preferably made by chemical vapor deposition processes. Such coatings find use in insulating glass for houses, in conductive glass for plasma TV screens, etc. The obtained coatings, which also make up a part of the invention, have high conductivity, high visible light transmittance, and low haze.

Description of the Related Art

Fluorine-doped tin oxide coatings are known to be conductive layers. Several chemical compositions and methods of production have been described in the literature regarding the manufacture such tin oxide coatings:

Japanese patent 75-61,415 utilizes a spray of chemicals present in a large amount of solvent, which produces significant technical and environmental problems, and which is not usable in a C.V.D.(Chemical Vapor Deposition) process.

European patent EP-A-0 112 780 describes a method using alkyl chloro tin and a gaseous alkyl chloro fluorocarbon which provides severe problems with regard to toxic waste by-products as well as difficulties in handling and controlling the gas.

U.S. patent 4,265,974 describes a method using tetramethyl tin, which is very toxic and explosive in air.

U.S. patent 4,293,594 describes a method using dimethyl tin difluoride, which is a powder too difficult to be vaporized.

U.S. patent 4,601,917 describes a method using a chloro tin compound doped with an organic fluorine compound selected from trifluoroacetic acid, trifluoroacetic anhydride, ethyl trifluoroacetoacetate, trifluoroethanol, ethyltrifluoroacetate and pentafluoropropionic acid. The presence of an oxygenated functional group in the molecule of the fluorine dopant promotes the formation of oxidized build-up before pyrolysis on the glass.

U.S. patent 4,857,095 describes a method using dibutoxydibutyl tin with trifluoroacetic acid. The presence of oxygen bonded to tin prevents the good formation of the tin oxide layer and gives numerous white deposits in the fume evacuation circuit.

Japanese patent JP-A-62,70247 describes a method using dibutyl tin (or dimethyl tin) di-trifluoroacetate or butyl tin tri-trifluoroacetate with trichlorobutyl tin or tetrachloro tin. The presence of chlorinated solvent in all solutions renders the composition dangerous and toxic. Moreover, it promotes the appearance of corrosive green deposits in the fume evacuation circuit.

French patent 93-05245 describes a method using a chlorinated organo tin compound doped with organo tin monofluoroalkanoate and a tetraorgano tin. The use of such a heavy fluorine dopant promotes the appearance of black deposits in the vapor circuit due to the high temperature of vaporization needed.

From the above description of the prior art, the need for a new composition useful in a CVD process giving improved conditions of vaporization, avoiding environmentally toxic waste and giving high conductivity, high visible light transmittance coatings on, for example, glass, is clear.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided herein a new liquid coating composition very well adapted for use in the chemical vapor deposition of a coating on glass substrates which:

- provides a very conductive layer, with low haze and high visible light transmittance.

-has a low temperature of vaporization which avoids decomposition, keeping the vaporization circuit essentially free of deposit.

-does not require and preferably does not contain any dangerous or toxic component.

-upon pyrolysis avoids significant production of corrosive dust and environmental pollutants.

The invention composition comprises a chlorinated organotin derivative and a polyfluoroalkyl or halo polyfluoroalkyl dopant.

DETAILED DESCRIPTION OF THE INVENTION

More specifically, the composition of the invention preferably comprises a mixture prepared by mixing together:

- 70% to 99% by weight of at least one organo-tin compound, preferably chlorinated organo-tin compound, wherein the tin atom is bonded to at least one carbon atom of a hydrocarbon chain;

- 1 % to 30% by weight of at least one polyfluoroalkyl, halo polyfluoroalkyl, polyfluoroalkenyl or halo polyfluoroalkenyl compound where "halo" is halogen other than fluorine (Cl, Br, etc.); and

Optionally up to 29 weight percent of an organic solvent.

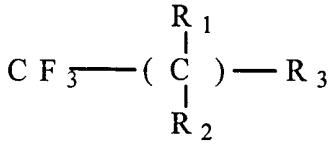
The preferred general formula of the organo- tin compound is:

$$R_x\ SnCl_{(4-x)} \qquad \text{Compound I}$$

wherein x is an integer which may vary from 1 to 4 (i.e., 1,2,3,4)and R represents a C_{1-8} alkyl or alkenyl group having one or more double bonds or a phenyl radical. Preferably, to avoid toxicological problems, R is a butyl radical. To limit the presence of carbon in the layer, x is preferably 1. These compounds are collectively referred to as (chlorinated) organotin compunds. The (chlorinated) organotin compound can also be a mixture of different compounds of the above formula.

The preferred general formula of the polyfluoroalkyl or alkenyl and halo polyfluoroalkyl or alkenyl compound is: $C_nF_mX_oH_p$, where n is at least 4 and preferably less than 25, m is 1-30, preferably 2 or greater, X is halogen other than fluorine, o is 0-30 and p is 0-52. When o is not zero the compound is a halo polyfluoroalkyl compound. When the carbon chain contains one or more double bonds the compounds are alkenyl compounds. These compounds are neutral organic compounds and include linear, branched and cyclic structures. The F, X and H atoms are substituents on the carbon atoms. For simplicity these alkyl and alkenyl compounds are described as (halo) polyfluoroalkyl compounds herein and preferably have boiling points of at least 50°C and more preferably from 50-200°C.

One group of preferred species is:



Compound II:

Where R_1, R_2 and R_3 are each independently hydrogen, halogen, C_{2-9} alkyl or C_{2-9} haloalkyl. The compound is a halo polyfluoroalkyl when any one or more of R_1, R_2 and R_3 are or contain halogen other than fluorine.

Preferably, compound II has a boiling point of from 50°C to 200°C.

The polyfluoroalkyl or halo polyfluoroalkyl compound can also be a mixture of one or more of these different compounds. Both the polyfluoro and halo polyfluoro compounds may be

present.

The composition according to the invention may also optionally comprise up to 29 weight % of an organic solvent such as xylene, methyl isobutyl ketone, dichloroethane, chloroform, CCl_4, etc. The solvent should preferably have a boiling point of 40 to 100°C. The solvent should be a liquid at STP. The organic solvent of the invention does not include the invention chlorinated organo-tin derivative, polyfluoroalkyl compound or halo polyfluoroalkyl compound.

The invention (chlorinated) organo tin compound, (halo) polyfluoro alkyl compound, and organic solvent are commercialiy available and/or within the skill of the ordinary artisan to obtain/synthesize.

The preferred way of producing a thin layer of fluorine doped tin oxide on a substrate with the invention composition is chemical vapor deposition. Useful substrates include glass, metal, etc. In this method, the invention liquid composition is vaporized in a continuous boiler at an effective temperature which temperature preferably is below 250°C. Then, the vapor can be mixed or carried out with oxygen, air (preferably hot air), and/or steam at a sufficient temperature to keep a complete vapor phase. The mixed vapor is directed on the substrate for pyrolysis. The temperature of the substrate must be higher than 400°C, preferably about (±20°C)500°C to 700°C.

With this method, a coating of fluorine doped tin oxide can be obtained having the following properties:

Thickness:	500Å to 9000Å, including 1000, 3000 and 5000Å
Sheet resistance:	5-250 ohms/square including 15, 25, 50, 100 and 150 ohms/square
Visible light transmittance:	> 70% such as > 80%, > 82%, >90%, etc.
Haze:	0% to 20% such as less than 0.5% (light diffused/total light transmitted)

Chemical vapor deposition processes are known to those of ordinary skill in the art, and the present invention method utilizing the invention composition is not limited to the example method specifically described.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment of the invention compound I is butyl tin trichloride ($BuSnCl_3$). Preferred species of halo polyfluoroalkyl and polyfluoroalkyl include one or more of the following species:

- C4F9I	Perfluorobutyl iodide	Bp: 72°C
- C5F11I	Perfluoroisopentyl iodide	Bp: 89-90°C
- C6F14	Perfluorohexane	Bp : 58-60°C
- C6F13H	1H,Perfluorohexane	Bp: 71°C
- C6F13Cl	Perfluorohexyl Chloride	Bp: 84-86°C
- C6F13I	Perfluorohexyl Iodide	Bp: 115-117°C
- C7F16	Perfluoroheptane	Bp: 80-85°C
- C7F13H	1H,Perfluoroheptane	Bp: 96-97°C
- C7F15Br	Perfluoroheptyl Bromide	Bp: 118-119°C
- C7F15I	Perfluoroheptyl Iodide	Bp: 137-138°C
- C8F16	Perfluoro-1,2-Dimethylcyclohexane	Bp: 102°C
- C8F18	Perfluorooctane	Bp: 99-100°C
- C8F17H	1H,Perfluorooctane	Bp: 110-112°C
- C8F17Br	Perfluorooctyl Bromide	Bp: 142°C
- C8F17I	Perfluorooctyl Iodide	Bp: 160-161°C
- C9F20	Perfluorononane	Bp: 125-126°C
- C9F19Br	Perfluorononyl Bromide	Bp: 159°C
- C10F20	Perfluorodecalin	Bp: 142°c

The invention compositions, which are within the skill of the ordinary artisan to make and use, preferably comprise (by weight) from 70% to 99% of the (chlorinated) organo tin compound such as compound I (including 75, 80, 85, 90 and 95%) and from 1% to 30% (including 5%, 10%, 15%, 20% and 25%) of the (halo) polyfluoroalkyl compound such as compound II. Solvent may be present in 29% or less, including 25%, 20%, 15%, 10%, 5%, greater than 0%, and 0%. compositions according to the invention may be prepared by mixing the necessary components together.

EXAMPLES

The Chemical Vapor Deposition installation and methodology described below was used

to produce fluorine doped tin oxide thin films on glass substrates:

-The invention composition is mixed and then pumped from a tank at a determined and regular flow rate, to a continuous boiler using a heating fluid at a fixed temperature of 225°C.

-The vapor produced in the boiler leaves the boiler at a temperature of about 205°C depending on the composition and the flow rate of the composition.

-The vapor is then mixed with hot air and steam. The temperature of the final mixture is maintained at about 205°C.

-This final gas mixture is then directed onto the surface of glass on a continuous production line of flat glass (float process).

-The temperature of the glass during contact is between 400°C and 700°C.

The following solutions were prepared by mixing together the listed ingredients in the indicated amounts (parts by weight). Solutions I, K and L must be agitated prior to use. The abbreviation MBTCL means mono butyl tin trichloride. MIBK is methyl isobutyl ketone.

A	Perfluoro n-Octyl Iodide	11.7
	MBTCL	58.7
	Xylene	20.6
B	Perfluoro n-Octyl Iodide	4.9
	MBTCL	77.7
	Xylene	17.4
C	Perfluoro n-Butyl Iodide	12.1
	MBTCL	84.9
	MIBK	3.0
D	Perfluoro n-Butyl Iodide	5.0
	MBTCL	95.0
F	Perfluoro n-Hexyl Iodide	4.9
	MBTCL	94.1
	MIBK	1.0
G	Perfluoro n-Octyl Bromide	2.36
	MBTCL	49.32
	Dichloro ethane	43.27
	Chloroform	5.05
I	Perfluoro Hexane	5.5
	MBTCL	82.0
	Tetrachloro methane	12.5

K	Perfluoro Hexane	10.0
	MBTCL	90.0
L	Perfluoro Octane	10.0
	MBTCL	90.0
M	Perfluorohexyl-Iodide	12.0
	MBTCL	85.0
	MIBK	3.0

The table below gives the different parameters used in the C.V.D. laboratory installation for 12 tests:

	Gas flow	Gas temp.	Air flow	Water flow
Solution G	0.825 L/mn	203°C	60 cfm	0.230 L/mn
Solution F	0.680 L/mn	204°C	60 cfm	0.205 L/mn
Solution K	0.860 L/mn	205°C	60 cfm	0.240 L/mn
Solution L	0.640 L/mn	204°C	60 cfm	0.190 L/mn
Solution F	0.820 L/mn	204°C	60 cfm	0.225 L/mn
Solution F	0.580 L/mn	206°C	60 cfm	0.185 L/mn
Solution A	0.700 L/mn	202°C	60 cfm	0.210 L/mn
Solution B	0.575 L/mn	204°C	60 cfm	0.190 L/mn
Solution C	0.850 L/mn	205°C	60 cfm	0.235 L/mn
Solution C	0.630 L/mn	206°C	60 cfm	0.200 L/mn
Solution D	0.880 L/mn	205°C	60 cfm	0.250 L/mn
Solution D	0.540 L/mn	208°C	60 cfm	0.180 L/mn

The table below gives the parameters used in the pilot test CVD installation.

Solution	Test	Chemical flow	Water flow	Air flow	Vapor temp.
M	1	0.450 L/mn	0.073 L/mn	80 cfm	150°C
M	2	0.724 L/mn	0.147 L/mn	90 cfm	170°C
M	3	0.870 L/mn	0.176 L/mn	80 cfm	190°C

The table below gives the film characteristics and performances measured on the coated

glass for laboratory tests.

	Film thickness	Sheet resistance	Visible transmittance	Haze
Test 1	3600 Å	23 ohm2	80%	0.6
Test 2	2800 Å	22 ohm2	83%	0.4
Test 3	4200 Å	22 ohm2	79%	0.6
Test 4	2850 Å	21 ohm2	84%	0.4
Test 5	4300 Å	19 ohm2	80%	0.5
Test 6	2800 Å	18 ohm2	83%	0.3
Test 7	2900 Å	23 ohm2	83%	0.3
Test 8	2700 Å	21 ohm2	85%	0.2
Test 9	4300 Å	20 ohm2	82%	0.4
Test 10	2900 Å	19 ohm2	84%	0.3
Test 11	4600 Å	21 ohm2	82%	0.5
Test 12	2800 Å	17 ohm2	85%	0.2

The Table below gives the film characteristics and performances from the coated glass produced using the pilot CVD installation.

Solution	Test	Film thickness	Sheet resistance in ohms per square	Visible transmittance	Haze	Emissivity
M	1	2300 Å	31.6	83.2%	0.3%	0.2
M	2	2600 Å	30	84.6%	0.4%	0.2
M	3	2700 Å	24.6	85.2%	0.6%	0.2

Performances given in the Tables above were measured with a Pacific Scientific Hazeguard XL-211, Perkin-Elmer Lamda-19 with integrating sphere, GE XRD-6 wavelength disperse x-ray, Perkin Elmer 983-G spectro photometer and four point probe.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims:

1. A composition comprising:

70-99 % by weight of at least one (chlorinated) organotin compound, 1-30 % by weight of at least one (halo) polyfluoroalkyl compound, and optionally an organic solvent in an amount up to 29 weight %.

2. The composition of Claim 1, wherein said at least one (chlorinated) organotin compound is a compound of the formula

$$R_xSnCl_{(4-x)}$$

wherein x is an integer of 1-4 and R is a C_{1-8} alkyl or alkenyl group, or a phenyl radical.

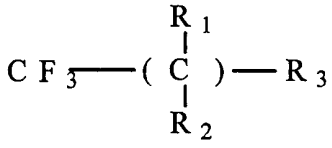
3. The composition of Claim 2, where R is butyl and X is 1.

4. The composition of Claim 1, wherein said at least one (halo) polyfluoroalkyl compound is a compound of the following formula:

$$C_nF_mX_oH_p$$

where n is 4-25, m is 1-30, o is 0-30, p is 0-52, and x is halogen other than fluorine.

5. The composition of Claim 1, wherein said at least one (halo) polyfluoroalkyl compound is a compound of the formula:



where R_1, R_2 and R_3 are each independently hydrogen, halogen, C_{2-9} alkyl or C_{2-9} haloalkyl.

6. The composition of Claim 1, comprising organic solvent.

7. The composition of Claim 1, wherein said (halo) polyfluoroalkyl compound is selected from the group consisting of:

perfluorobutyl iodide, perfluoroisopentyl iodide, perfluorohexane, perlfuorohexane, perfluorohexyl chloride, perfluorohexyl iodide, perfluoroheptane, perfluoroheptyl bromide , perfluoroheptyl iodide, perfluoro-1,2-dimethylcyclohexane, perfluorooctane, perfluorooctane, perfluorooctyl bromide, perfluorooctyl iodide, perfluorononane, perfluorononyl bromide, perfluorodecalin.

8. The composition of Claim 2, wherein said (halo) polyfluoroalkyl compound is selected from the group consisting of:

perfluorobutyl iodide, perfluoroisopentyl iodide, perfluorohexane, perlfuorohexane, perfluorohexyl chloride, perfluorohexyl iodide, perfluoroheptane, perfluoroheptyl bromide , perfluoroheptyl iodide, perfluoro-1,2-dimethylcyclohexane, perfluorooctane, perfluorooctane, perfluorooctyl bromide, perfluorooctyl iodide, perfluorononane, perfluorononyl bromide, perfluorodecalin.

9. The composition of Claim 3, wherein said (halo) polyfluoroalkyl compound is selected from the group consisting of:
perfluorobutyl iodide, perfluoroisopentyl iodide, perfluorohexane, perlfuorohexane, perfluorohexyl chloride, perfluorohexyl iodide, perfluoroheptane, perfluoroheptyl bromide , perfluoroheptyl iodide, perfluoro-1,2-dimethylcyclohexane, perfluorooctane, perfluorooctane, perfluorooctyl bromide, perfluorooctyl iodide, perfluorononane, perfluorononyl bromide, perfluorodecalin.

10. The composition of Claim 4, wherein said (halo) polyfluoroalkyl compound is selected from the group consisting of:
perfluorobutyl iodide, perfluoroisopentyl iodide, perfluorohexane, perlfuorohexane, perfluorohexyl chloride, perfluorohexyl iodide, perfluoroheptane, perfluoroheptyl bromide , perfluoroheptyl iodide, perfluoro-1,2-dimethylcyclohexane, perfluorooctane, perfluorooctane, perfluorooctyl bromide, perfluorooctyl iodide, perfluorononane, perfluorononyl bromide, perfluorodecalin.

11. The composition of Claim 6, wherein said (halo) polyfluoroalkyl compound is selected from the group consisting of:
perfluorobutyl iodide, perfluoroisopentyl iodide, perfluorohexane, perlfuorohexane, perfluorohexyl chloride, perfluorohexyl iodide, perfluoroheptane, perfluoroheptyl bromide , perfluoroheptyl iodide, perfluoro-1,2-dimethylcyclohexane, perfluorooctane, perfluorooctane, perfluorooctyl bromide, perfluorooctyl iodide, perfluorononane, perfluorononyl bromide, perfluorodecalin.

12. A method of preparing a fluorine-doped tin oxide film on a substrate, comprising contacting a hot substrate with the composition of Claim 1 in the vapor state, wherein said substrate is at a temperature of ≥ 400°C.

13. A method of preparing a fluorine-doped tin oxide film on a substrate, comprising contacting a hot substrate with the composition of Claim 2 in the vapor state, wherein said substrate is at a temperature of ≥ 400°C.

14. A method of preparing a fluorine-doped tin oxide film on a substrate, comprising contacting a hot substrate with the composition of Claim 3 in the vapor state, wherein said substrate is at a temperature of ≥ 400°C.

15. A fluorine-doped tin oxide film prepared according to the method of Claim 12.

16. A fluorine-doped tin oxide film prepared according to the method of Claim 13.

17. A fluorine-doped tin oxide film prepared according to the method of Claim 14.

INTERNATIONAL SEARCH REPORT

Int ational Application No
PCT/IB 99/01245

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/40 C03C17/245

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C C03C

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 practical. search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 590 096 A (LINDNER GEORGE H) 20 May 1986 (1986-05-20) column 3, line 46 -column 6, line 25; claims 1,2	1-17
X	WO 86 06658 A (M & T CHEMICALS INC) 20 November 1986 (1986-11-20) page 6, line 7 - line 29	1-3,5, 15-17
A	EP 0 027 403 A (SAINT GOBAIN VITRAGE) 22 April 1981 (1981-04-22) page 2, line 9 - line 21	1-17
A	US 4 547 400 A (MIDDLETON DARYL J ET AL) 15 October 1985 (1985-10-15) column 1, line 52 -column 2, line 46	1-17

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int national Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document. with indication.where appropriate. of the relevant passages	Relevant to claim No.
A	US 4 705 701 A (AKHTAR MASUD) 10 November 1987 (1987-11-10) examples 1,2 -----	1-17

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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