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(71) **Applicant** *(for all designated States except US)*: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **MAURER, Marc** [FR/FR]; rue de la Pyramide 8, F-68128 Village-Neuf (FR). **HÜGIN, Max** [CH/CH]; Zielweg 256, CH-4497 Rünenberg (CH). **RAIMANN, Thomas** [CH/CH]; Bodenackerstrasse 15D, CH-4334 Sisseln (CH). **FEILER, Leonhard** [DE/DE]; Ötlingerblick 6, 79589 Binzen (DE). **INDERBITZIN, Bruno** [FR/FR]; 2 Rue de Ferrette, F-68480 Bouxwiller (FR). **FUCHS, André** [DE/DE]; Im Kirschgarten 19, 79418 Schliengen-Obereggenen (DE).

(74) **Common Representative**: **BASF SE**; IP Department, P.O. Box, CH-4002 Basel (CH).

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(54) **Title**: PREPARATION OF A PHOTOCHROMIC INK

(57) **Abstract**: The present invention relates to a photochromic ink, the process for its preparation which is based on a spiropyran powder obtainable by melting, cooling and crushing, and to a new form of a spiropyran obtainable thereby. Said process to prepare a photochromic ink comprises the steps of a) heating and melting the spiropyran at a temperature below 250 C, b) cooling the melt to obtain a solidified spiropyran, c) crushing the solidified spiropyran to obtain a powder, d) optionally adding the powder to a binder providing the basis for the photochromic ink.

Preparation of a photochromic ink

The present invention relates to a photochromic ink, the process for its preparation which is based on a photochromic spiropyran powder obtainable by melting, cooling and crushing, and to a new form of a photochromic spiropyran obtainable thereby.

The use of photochromic inks or dyes is well known. By "photochromic ink" is meant a formulation formed as fluid ink which changes color when exposed to UV light radiation and provides a sufficiently high color density for use in the printing processes.

The International Application WO2005075978 (Freshpoint) describes the preparation of solvent-based or water-based printing inks comprising a spiropyran, an acrylate polymer as binder, a solvent or water and additives. The spiropyran is added as finely ground powder.

Spiropyrans used for preparing printing inks for time temperature indicators have to be easily dispersible. Therefore a small particle size of the spiropyran is required, for example obtained by intensively milling using standard bead mills. This method has at least two drawbacks. First, the milling operation is a time-intensive process, as long milling times are required to produce small enough particles to enable the formation of a stable dispersion. Second, the milling operation can not be used for all spiropyrans as some spiropyrans irreversibly change their color during milling.

A good dispersibility is needed to obtain a high color strength. The use in aqueous and solvent-based systems is desired.

The problem underlying the present invention is to reduce the milling time and to prepare an easily activable spiropyran which can be easily converted into a colored spiropyran having a high color strength. “Easily activable” or “easily converted” means that only short exposure to UV light is required.

It has been found that spiropyrans after melting and re-solidifying show different properties compared to crushed spiropyrans obtained by milling. First, it is possible to combine the spiropyran powder with a basic ink formulation without intensive milling. Second, a very high color strength is obtained after activation with UV light. In order to reach the same color

strength milled spiropyrans need a longer exposure time (circa 10 times longer) with UV light than the melted/re-solidified products.

Thus, the invention relates to a process to prepare a photochromic ink comprising the steps of

a) heating and melting a spiropyran, i.e. a photochromic spiropyran at a temperature below 250 °C, i.e. heating a photochromic spiropyran until it has melted,
b) cooling the melt to obtain a solidified spiropyran,
c) crushing the solidified spiropyran to obtain a powder,
d) optionally adding the powder to a binder providing the basis for the photochromic ink.

The invention further relates to a photochromic ink obtainable according to the process of claim 1.

The invention further relates to a photochromic spiropyran in the form of a powder which, after dispersion in a printing ink, has at least the double color strength than known forms of the same spiropyran, said powder being obtainable by

a) heating and melting a photochromic spiropyran at a temperature below 250 °C, i.e. carefully heating the spiropyran until it has melted,
b) cooling the melt to obtain a solidified spiropyran, and
c) crushing the solidified spiropyran to obtain a powder.

The reason for the unique property of the new form of a spiropyran is not entirely clear. It may be due to the particle size. Spiropyrans of similar particle size may e.g. not be accessible by conventional methods due to reaggregation of small particles in the milling operation.

The inventive process allows the preparation of easily activable time temperature indicators in powder form which can be used in various ink formulations.

The decomposition temperature of spiropyrans is below 250 °C, i.e. all spiropyrans so far tested by the present inventors at least start decomposing below or even far below 250 °C. A certain degree, e.g. up to 20%, 30%, 40% or even 50%, of decomposition is acceptable since the gain in color strength by the inventive process more than compensates for the loss

of intact spiropyrans by decomposition. However, some spiropyrans tend to decompose rather rapidly, some even explosively. Hence, due care should be taken not to raise the temperature more than is necessary to obtain a complete melt or not to use explosive spiropyrans in the process of the present invention, especially not in larger scale. Spiropyrans which are suitable for being used in the process of the present invention can easily be detected and selected, e.g. by heating an undangerously small amount of them until they melt and watching the decomposition behaviour.

The preferred manner of carrying out process step a) above is to heat the spiropyran until it has melted, i.e. to heat it only slightly, e.g. 2, 5 or 10 °C above its melting point which is usually in the range of 140-200 °C, especially 150-190 °C. Preferably, heating is continued until melting is complete, i.e. all of the spiropyran has melted, but in order to avoid circumvention of the patent protection the respective patent claim comprises also those modifications of the process wherein only a substantial portion, e.g. 10, 20, 30, 40, 50, 60, 70, 80 or 90 per cent (percent), of the spiropyran has melted.

The solidified spiropyran is in a transparent form.

Solidified is crystalline or semi amorphous. The term "semi-amorphous" herein means a spiropyran having an intermediate structure of an amorphous structure and a crystalline structure.

Cooling means, for example, cooling to room temperature or a temperature below room temperature and comprisesalso shock cooling. Shock cooling is preferably performed by pooring the melt on solid carbon dioxide (also called dry ice or carbon dioxide snow) or into liquid nitrogen whereupon the melt usually splits into tiny pieces.

The melting is carried out using any method of heat transfer, for example the melting is formed by heating using an oil bath, by melt extrusion, by radiation, e.g. NIR/IR radiation, heating using a hot air technology, heating by using a cold plasma and the like.

A short heating treatment is preferred to avoid the decomposition of the spiropyrans.

Polymeric binders for inks include all polymers known to be used in inks, e.g. homopolymers, copolymers (random or block-copolymers) or mixtures thereof including polymers of acrylic acid or methacrylic acid, acrylates or methacrylates (e.g. methyl acrylate or methyl methacrylate), styrene, acrylamide, vinyl acetate, vinyl alcohol, vinyl chloride, polyurethanes, cellulose nitrate, carboxymethyl cellulose. Preferred is a water-soluble or water- dispersible acrylic polymer. The binder is thus preferably an acrylic binder.

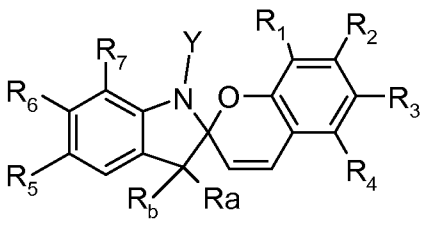
Inks contain a variety of additives to eliminate foaming, dispersion of pigments, rheological modifiers, and slip agents.

The inks comprise a total content of spiropyran of from 1 to 20 % by weight, preferably 1.5-20% by weight, 2-20% by weight, 3-20% by weight based on the total weight of the ink.

The spiropyran-dispersed ink composition can be produced by employing various methods which have so far conventionally been known. For example, it can readily be obtained by blending the respective components (binder, additive, spiropyran powder) and mixing and stirring them by means of a stirrer such as a dissolver or mixing and crushing them by means of a ball mill.

The spiropyran compound is for example a spiropyran as disclosed (including processes for its manufacture) in WO 2008/083925 A1 or WO 2005075978 A2 (Freshpoint), or a spiropyran as disclosed in the European Application EP08156605 (Ciba), filed May 21, 2008 (corresponding to PCT/EP2009/05564 filed May 11, 2009 and published as WO2009141237 A1), all of which publications are incorporated herein by reference.

This is especially a spiropyran derivative of formula I:



(I)

wherein

R_1 is hydrogen, -C_1-C_{18} alkoxy, -C_1-C_{18} alkylthio, halogen, -C_1-C_{18} alkyl, -NO_2 or a phenyl radical, like preferably phenyl;

R_2 is hydrogen, -C_1-C_{18} alkoxy or NO_2;

R_3 is NO_2 or halogen;

R_4 is hydrogen, -C_1-C_{18} alkoxy or halogen;

R_5 is hydrogen, halogen, -C_1-C_{18} alkoxy, -COOH, -COO-C_1-C_{18}alkyl, -CF_3 or phenyl;

R_6 is hydrogen or R_6 and R_7 form together a phenyl ring;

R_7 is hydrogen;

R_a is hydrogen or -C_1-C_6 alkyl;

R_b is hydrogen or -C_1-C_6 alkyl, or together with R_a form a 5-6 membered ring;

Y is phenyl or benzyl wherein the phenyl or benzyl group may be substituted by one or more groups selected from NO_2, fluorine, bromine, chlorine, CF_3 or phenyl and may carry an annealed benzo ring, or

Y is–CH_2-COO- C_1-C_{18}alkyl or –CH_2-COOH or –CH_2-CO-N(R_{10})-R_9; or –CH_2-CO-N(R_{10})-L-N(R_{10}) CO-CH_2- ; wherein

R_9 is hydrogen, C_1-C_{18}alkyl , phenyl, mesityl, phenyl once or more than once substituted by halogen, -CF_3, C_1-C_6alkyl, -C_1-C_6 alkoxy, carboxy, -COO-C_1-C_6alkyl, -S-phenyl or -CO-phenyl;

R_{10} is hydrogen, C_1-C_{18}alkyl;

L is 1,3 phenylene or 1,4 phenylene wherein the phenylene linker is optionally substituted by once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro; or L is naphthalene, biphenylene or phenylene-O-phenylene wherein the naphthalene, biphenylene or phenylene-O-phenylene linker is optionally substituted once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro.

Phenyl or benzyl Y carrying an is napthyl or napthylmethyl. Preferably, Y does not carry an annealed benzo ring.

Preferences

Preferred are compounds of the formula I wherein

R_1 is hydrogen, -C_1-C_{18} alkoxy, -C_1-C_{18} alkylthio, halogen, -C_1-C_{18} alkyl or -NO_2;

R_2 is hydrogen or -C_1-C_{18} alkoxy;

R_3 is NO_2 or halogen;

R_4 is hydrogen, -C_1-C_{18} alkoxy or halogen;

R_5 is hydrogen, halogen, -C_1-C_{18} alkoxy, -COOH, -COO-C_1-C_{18}alkyl, -CF_3 or phenyl;

R_6 is hydrogen or R_6 and R_7 form together a phenyl ring;

R_7 is hydrogen;

R_a is hydrogen or -C_1-C_6 alkyl;

R_b is hydrogen or -C_1-C_6 alkyl, or together with R_a form a 5-6 membered ring;

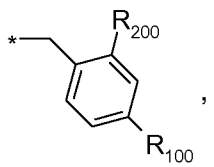
Y is phenyl or benzyl wherein the phenyl or benzyl group may be substituted by one or more groups selected from fluorine, bromine, chlorine, CF_3 or phenyl or Y is–CH_2-COO- C_1-C_{18}alkyl or –CH_2-COOH or –CH_2-CO-N(R_{10})-R_9; or –CH_2-CO-N(R_{10})-L-N(R_{10}) CO-CH_2- ;wherein

R_9 is hydrogen, C_1-C_{18}alkyl , phenyl, mesityl, phenyl once or more than once substituted by halogen, -CF_3, C_1-C_6alkyl, -C_1-C_6 alkoxy, carboxy, -COO-C_1-C_6alkyl, -S-phenyl or -CO-phenyl;

R_{10} is hydrogen, C_1-C_{18}alkyl;

L is 1,3 phenylene or 1,4 phenylene wherein the phenylene linker is optionally substituted by once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro; or L is naphthalene, biphenylene or phenylene-O-phenylene wherein the naphthalene, biphenylene or phenylene-O-phenylene linker is optionally substituted once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro.

Preferred are compounds of the formula I wherein

Y is 

,

R_1 is C_1-C_6alkoxy, preferably methoxy,

R_2 is hydrogen,

R_3 is NO_2,

R_4 is hydrogen,

R_5 is hydrogen or C_1-C_6alkoxy,

R_6 is hydrogen,

R_7 is hydrogen,

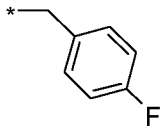
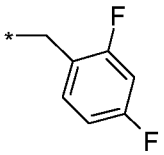
R_a is methyl,

R_b is methyl,

R_{100} is NO_2, bromine, fluorine or CF_3, preferably bromine, fluorine or CF_3,

R_{200} is hydrogen or fluorine.

Especially preferred is a compound of the formula I wherein

Y is nitro-benzyl, like especially 4-nitro-benzyl, or  or  ;

preferably Y is 4-fluoro-benzyl or 2,4-difluoro-benzyl,

R_1 is methoxy,

R_2 is hydrogen,

R_3 is NO_2,

R_4 is hydrogen,

R_5 is hydrogen

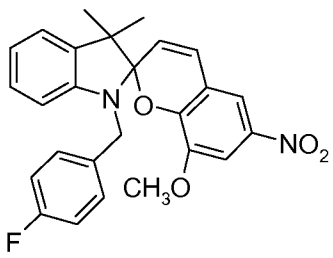
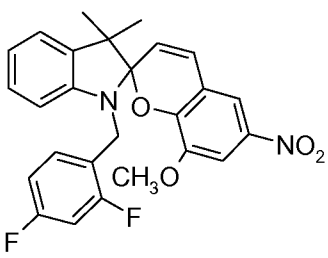
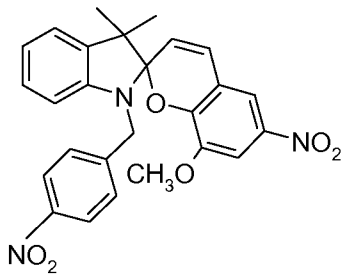
R_6 is hydrogen,

R_7 is hydrogen,

R_a is methyl,

R_b is methyl,

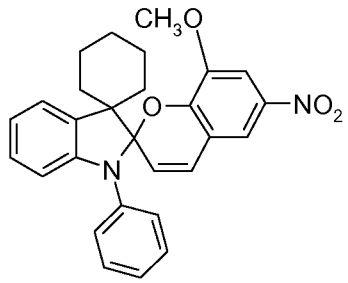
The preferred compound has the following formula

 or  or 

The spiropyran compounds are molten and re-solidified by cooling to room temperature. The re-solidified spiropyran can easily be dispersed in an ink formulation. The milling time is reduced by factor 5 compared to unmolten spiropyrans. The exposure time of the ink formulation by UV radiation is less (approximately 4-40%, preferably 4-10%) compared to an ink formulation containing an unmolten spiropyran.

Furthermore preferred is a compound of the formula I wherein Ra and Rb together form a hexylene ring, Y is phenyl, R_1 is methoxy, R_2 is hydrogen, R_3 is nitro, R_4 is hydrogen, R_5 is

hydrogen, R_6 is hydrogen R_7 is hydrogen. This preferred compound has the following formula



MH1188

Furthermore preferred are compounds of the formula I

wherein Y is $–CH_2$-COR,

R_1 is C_1-C_6alkoxy, C_1-C_6alkylthio, or a phenyl radical, like especially phenyl, preferably R_1 is C_1-C_6alkoxy or C_1-C_6alkylthio,

R is $–C_1$-C_6alkoxy or -NHR_9 wherein R_9 is phenyl, phenyl once or more than once substituted by halogen, -CF_3, C_1-C_6alkyl, -C_1-C_6 alkoxy, -S-phenyl or -CO-phenyl,

R_2 is hydrogen,

R_3 is NO_2,

R_4 is hydrogen,

R_5 is hydrogen,

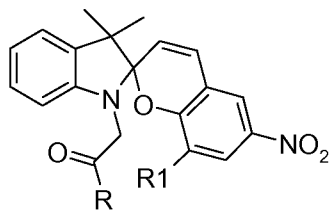
R_6 is hydrogen,

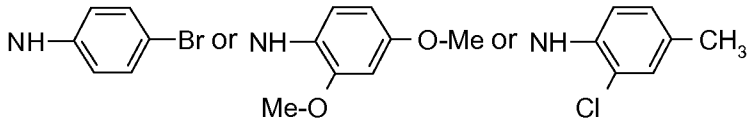
R_7 is hydrogen,

R_a is methyl and

R_b is methyl.

These compounds can be expressed by the following formula Ia

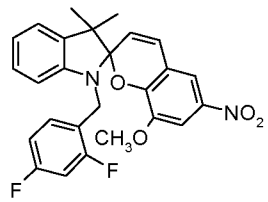


Especially preferred are further compounds of the formula Ia wherein R_1 is methoxy or ethoxy and R is  .

Examples

Example 1: melting

1g 1'-(2,4-Difluorbenzyl),3',3'-dimethyl-6-nitro-8-methoxy(2H-1-benzopyran-2,2'-2H-indol) (LF3233)



is heated in a glass tube at 160°C for 5 minutes. The molten mass is cooled to room temperature and pulverized. The powder is then added to an aqueous based basic ink formulation using a planetary mill (available from Fritsch GmbH, Planetary Fritsch Pulverisette 7) to obtain a printing ink.

The basic ink formulation is described below.

The printing ink is then applied to a paper using a wiper. The film thickness is approximately 12 µm. The label obtained is activated using UV light.

The Table below shows that the molten and re-solidified spiropyran according to the invention needs only 1/10 of the UV Dosis to reach the same color strength as the unmolten spiropyran. The radiation time is reduced from 2 seconds to 0.2 seconds.

The values L, a and b used in the present text are informal abbreviations of the coordinates of the CIE color space L*, a* and b* and should not be mixed up with the Hunter values L, a and b. L (and L*) define the lightness axis of the CIE color space with 0 meaning black and 100 meaning white; a (and a*) define the location on the red - green axis (positive values are red, negative values are green, and 0 is neutral); and b (and b*) define the location on the blue – yellow axis (positive values are yellow, negative values are blue, and 0 is neutral).

The starting color values (uncharged) of the unmolten and the molten spiropyran are slightly different due to a slight discoloration during the melting process.

Unmolten 2 seconds activated:

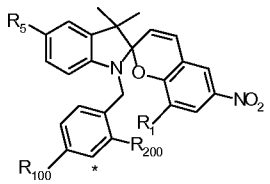
	L	a	b
uncharged	86.74	-0.14	4.27
charged	44.6	-0.54	-38.43

molten 0,2 seconds activated:

L	a	b
81.84	1.51	1.33
42.36	-4.94	-42.01

The bleaching kinetic is the same for both products.

The following spiropyrans having a benzylic group Y are treated analogously as described in Example 1.

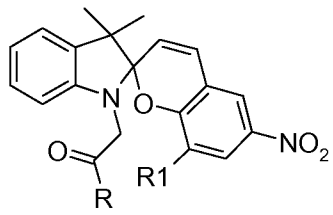


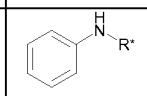
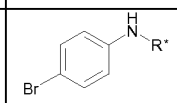
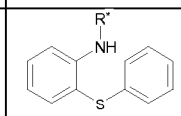
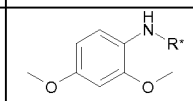
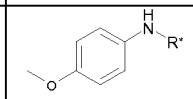
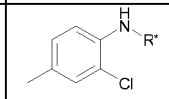
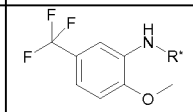
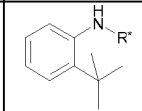
Lab No.	R_{100}	R_{200}	R_1	R_5	Melting Temp (°C)	Melting Time (min)	Exposure time to UV radiation (s)	L-value
LF3206	Br	H	OMe**	H	-	-	10	53
					195	1	4	34
LF3391	H	H	OMe	H	-	-	10	41
					170	1	4	29
LF2923	**	H	OMe	H	-	-	10	56
					170	5	4	38
LF2807	F	H	OMe	H	-	-	10	39
					155	1	0.4	39
FP152	CF_3	H	OMe	H	-	-	10	27
					160	5	10	11
FP258	CF_3	H	OMe	OMe	-	-	10	44
					160	5	10	16
FP220	I	H	OMe	H	-	-	10	37
					185	5	10	22

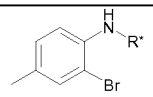
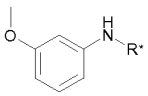
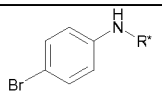
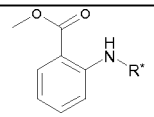
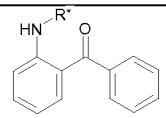
* LF2923 carries a benzo ring which is annealed to the C-atom carrying the substituent R_{100} and the C-atom marked with * in the above formula.

** OMe means methoxy, i.e. OCH_3 .

The following spiropyrans having an ester or amid group Y are treated analogously as described in Example 1.



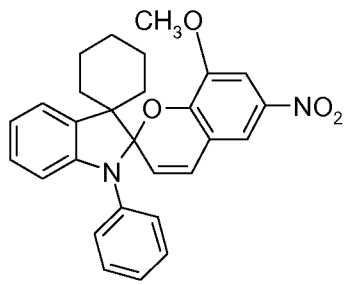
Lab No.	R	R_1	Melting Temp (°C)	Melting Time (min)	Exposure time to UV radiation (s)	L-value
LF3721	$-OCH(CH_3)_2$	OMe (OCH_3)	-	-	10	31
			150	5	4	14
LF3471		OMe	-	-	10	67
			190	1	4	40
LF3838		OMe	-	-	10	63
			180	1	4	38
LF3847		OMe	-	-	10	85
			180	1	10	50
LF4001		OMe	-	-	10	77
			180	1	1	44
LF3849		OMe	-	-	10	69
			180	1	1	40
LF4005		OMe	-	-	10	68
			180	1	1	35
LF4009		OMe	-	-	10	77
			180	1	10	43
LF3550		OMe	-	-	10	73
			180	1	4	44

Lab No.	R	R_1	Melting Temp (°C)	Melting Time (min)	Exposure time to UV radiation (s)	L-value
LF4022		OMe	-	-	10	70
			180	1	1	32
LF4026		OMe	-	-	10	71
			180	1	10	38
LF4032	-OCH(CH_3)$_2$	OEt**	-	-	10	82
			180	1	10	55
LF4033	-OCH(CH_3)$_2$	SMe***	-	-	10	50
			180	1	1	32
LF4035		OEt**	-	-	10	76
			180	1	1	42
LF4028		OMe	-	-	10	76
			180	1	4	59
LF4021		OMe	-	-	10	74
			180	1	4	61

R* indicates the position of the free valency forming the linkage to the rest of the spiropyran molecule.

** OEt = ethoxy = -O-CH_2-CH_3 *** SMe = methylthio = -S-CH_3

The following spiropyran compound is treated analogously as described in Example 1

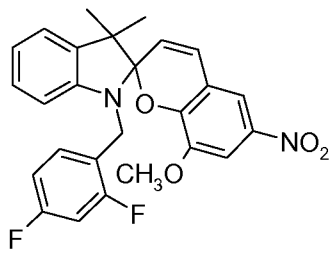


MH1188

Unmolten 3 seconds activated molten 0.3 seconds activated

	L	a	b
uncharged	88.2	0.57	1.03
charged	63.6	1.05	1.8

L	a	b
83.6	1.02	2.1
44.17	-36.96	-30.53

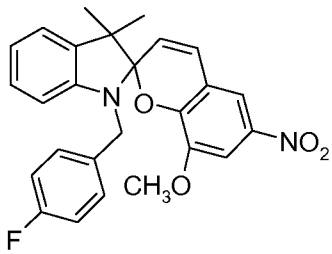
The following spiropyran compound  is molten in a glass tube at 171°C for 5 minutes and further treated according to Example 1.

unmolten 2 seconds activated

	L	a	b
uncharged	86.74	-0.14	4.27
charged	44.6	-0.54	-38.43

molten 0,2 seconds activated

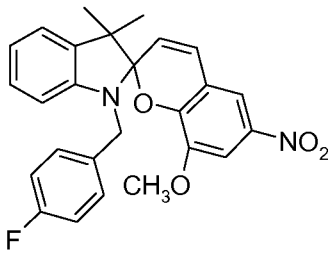
L	a	b
81.84	1.51	1.33
42.36	-4.94	-42.01

A Collin ***Teachline*** extruder E 20 T is heated to 160°C. The extruder is loaded with 500g of the following spiropyran (LF2807)  and extruded out in 25 min.

The spiropyran is molten during the extrusion process and exites out as a high viscous liquid which is then cooled. Glassy plates are formed. The plates are crushed and added to an aqueous based basic ink formulation using a planetary mill (available from Fritsch GmbH,Planetary Fritsch Pulverisette 7) to obtain a printing ink.

molten 2 seconds activated

	L	a	b
uncharged	89.7	-0.77	2.7
charged	29.97	-0.57	-36.95

3 g of the following spiropyran  is molten in a microwave (800W) for 2 minutes. The molten mass is cooled to room temperature and pulverized. The powder is then added to an aqueous based basic ink formulation using a planetary mill (available from Fritsch GmbH,Planetary Fritsch Pulverisette 7) to obtain a printing ink

molten 2 seconds activated

	L	a	b
uncharged	92.7	-0.58	1.8
charged	33.4	-0.62	-36.73

Preparation of the water based printing ink which contains 10% spiropyran (TTI)

Step 1: Basic printing ink

20g Glascol® LS-16 (Ciba AG) (acrylic copolymer in an aqueous solution)

20g Joncryl® 74 (BASF AG)

0.25g TEGO® Foamex 845 als antifoaming agent (Evonik Industries AG)

Step 2: preparation of the TTI-printing ink:

1g spiropyran (TTI)

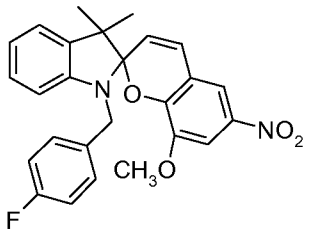
9g Basic printing ink

35g zirconium oxide -balls having a diameter of 0.7-0.9mm

Milling for 15min at 650 rpm (rounds per minute) using a planetary mill (Planetary Fritsch Pulverisette 7 available from Fritsch GmbH, Germany).

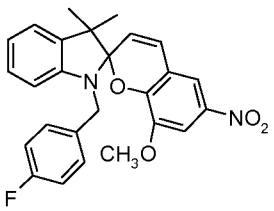
Leaving the printing ink over night and separate the balls.

Example 2: dispersing

The raw, i.e. crystalline and unmilled compound of the formula 

(before melting step) is dispersed in the basic printing ink formulation described above according to the usual dispersion process described above, i.e. using a planetary mill (Planetary Fritsch Pulverisette 7 available from Fritsch GmbH, Germany) and milling at 650 rounds per minute (rpm), and the coloristical properties (especially L-Value -> color development) are checked after 5, 15 and 30 minutes dispersion time. The color development after irradiation with UV light (cf. Example 3) is poor and very slow.

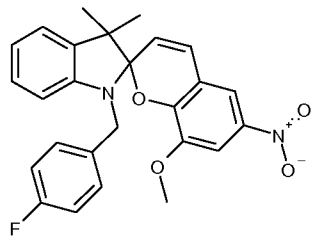
	L	a	b
uncharged	93.84	-1	2.75
5' Dispersion	73.79	-4.65	-4.25
15' Dispersion	63.79	-8.72	-12.72
30' Dispersion	59.24	-7.34	-10

The same compound  after melting step is also dispersed according to the usual dispersion process and the coloristical properties (especially L-Value -> color development) are checked after 5, 15 and 30 minutes dispersion time. The color development after irradiation with UV light (cf. Example 3) shows that a very high and constant L-value is already obtained after only 5 minutes processing time (dispersion time).

	L	a	b
uncharged	91.77	-0.83	1.89
5' Dispersion	22	2.17	-39.47
15' Dispersion	21.74	2.83	-40.97
30' Dispersion	22.94	-1.97	-37.93

Example 3: color strength comparison of crystalline, milled and molten LF2807

Synthesis of crystalline LF2807 (as described on page 19 of WO 2008/083925 A1) having the structure:



Step 1) A solution of 2,3,3-trimethylindolenine (5.0 g, 31.4 mmol) and 4-fluorobenzylbromide (3.0 g, 15.7 mmol) in dry toluene 30 ml is stirred overnight at 80-85°C. The mixture is cooled to room temperature, filtered through a glass filter, washed with diethyl ether and dried under reduced pressure. The crude product is dissolved in CH_2Cl_2 and treated with 5% aqueous NaOH under stirring for 30 minutes. The organic phase is separated, dried over Na_2SO_4, passed through a short alumina column in equal parts per volume of hexane-CH_2Cl_2 and evaporated giving rise to a corresponding free base, which is immediately dissolved in 10 ml ethanol containing a few drops of triethylamine.

Step 2) A solution of 1-(4'-fluorobenzyl)-3,3-dimethyl-2-methylene-indoline (2.7 g, 10.0 mmol) and 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (3.6 g, 13.0 mmol) is refluxed in 25 ml ethanol for 2 hours, cooled to room temperature, filtered, triturated with 1% triethylamine (in water), washed with water, crystallized from ethanol, and dried under reduced pressure yielding crystalline LF2807.

Color strength comparison:

(A): Crystalline LF2807 is stirred in 5% loading in the basic printing ink described above using a standard Teflon made disk-stirrer (100 rpm) for 10 minutes.

(B) Crystalline LF2807 is dispersed and milled in 5% loading in the printing ink described above using a perl mill (pulverisette) with zirconium oxide beads (650 rpm) for 10 minutes.

(C) Crystalline LF2807 is molten, re-solidified, dispersed and milled in 1% loading in the printing ink described above using a perl mill (pulverisette) with zirconium oxide beads (650 rpm) for 10 minutes.

All produced inks are drawn on paper using a #2 doctor blade resulting in an ink thickness of aproximately 12µm (wet). The prints are charged subsequently with UV light of 365 nm for 1 or 10 seconds as specified in the following table and the color is measured using a colorimeter.

The following results are obtained:

Experiment	starting L-value	Charging	L-value after loading	color strength (approximately)
A	96	10 seconds	91	extremely low
B	87	1 second	45	100%, comparison
C	85	1 second	46	~500%

As can be seen above, after dispersion in the printing ink by identical treatment in the perl mill, the molten, re-solidified and milled LF2807 (Experiment C) exhibits about the same L-value as the unmolten and milled LF2807 (Experiment B) despite the fact that the concentration of the active material in Experiment C is 5 times lower. Therefore the color strength for the molten, re-solidified and milled LF2807 is 500% as compared to the unmolten and milled LF2807 for which the color strength is set as 100%.

The color strength of crystalline LF2807 which is not milled, but only stirred in the printing ink is extremely low.

Claims

1. A process to prepare a photochromic ink comprising the steps of

a) heating and melting the spiropyran at a temperature below 250 °C,

b) cooling the melt to obtain a solidified spiropyran,

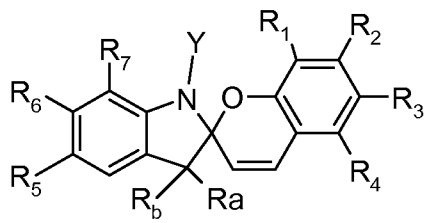
c) crushing the solidified spiropyran to obtain a powder, and

d) adding the powder to a binder providing the basis for the photochromic ink.

2. A photochromic ink obtainable according to the process of claim 1.

3. A process according to claim 1 wherein the binder is water-soluble or water- dispersible acrylic polymer.

4. A process according to claim 1 wherein the spiropyran is a compound of the formula I:



(I)

wherein

R_1 is hydrogen, -C_1-C_{18} alkoxy, -C_1-C_{18} alkylthio, halogen, -C_1-C_{18} alkyl, -NO_2 or a phenyl radical;

R_2 is hydrogen, -C_1-C_{18} alkoxy or NO_2;

R_3 is NO_2 or halogen;

R_4 is hydrogen, -C_1-C_{18} alkoxy or halogen;

R_5 is hydrogen, halogen, -C_1-C_{18} alkoxy, -COOH, -COO-C_1-C_{18}alkyl, -CF_3 or phenyl;

R_6 is hydrogen or R_6 and R_7 form together a phenyl ring;

R_7 is hydrogen;

R_a is hydrogen or -C_1-C_6 alkyl;

R_b is hydrogen or -C_1-C_6 alkyl, or together with R_a form a 5-6 membered ring;

Y is phenyl or benzyl wherein the phenyl or benzyl group may be substituted by one or more groups selected from NO_2, fluorine, bromine, chlorine, CF_3 or phenyl or

Y is–CH_2-COO- C_1-C_{18}alkyl or –CH_2-COOH or –CH_2-CO-N(R_{10})-R_9; or –CH_2-CO-N(R_{10})-L-N(R_{10}) CO-CH_2- ;wherein

R_9 is hydrogen, C_1-C_{18}alkyl , phenyl, mesityl, phenyl once or more than once substituted by halogen, -CF_3, C_1-C_6alkyl, -C_1-C_6 alkoxy, carboxy, -COO-C_1-C_6alkyl, -S-phenyl or -CO-phenyl;

R_{10} is hydrogen, C_1-C_{18}alkyl;

L is 1,3 phenylene or 1,4 phenylene wherein the phenylene linker is optionally substituted by once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro; or L is naphthalene, biphenylene or phenylene-O-phenylene wherein the naphthalene, biphenylene or phenylene-O-phenylene linker is optionally substituted once or more than once by halogen, -CF_3, C_1-C_{18}alkyl, -C_1-C_{18} alkoxy, carboxy , -COO-C_1-C_{18}alkyl, -$CONH_2$, -CON(C_1-C_{18}alkyl)$_2$, nitro.

5. A process according to claim 4, wherein the spiropyran is a compound of the formula I wherein

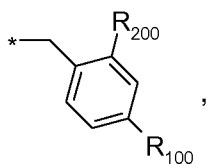
R_1 is hydrogen, -C_1-C_{18} alkoxy, -C_1-C_{18} alkylthio, halogen, -C_1-C_{18} alkyl, or NO_2,

R_2 is hydrogen or -C_1-C_{18} alkoxy,

Y is phenyl or benzyl wherein the phenyl or benzyl group may be substituted by one or more groups selected from NO_2, fluorine, bromine, chlorine, CF_3 or phenyl or Y is–CH_2-COO- C_1-C_{18}alkyl or –CH_2-COOH or –CH_2-CO-N(R_{10})-R_9; or –CH_2-CO-N(R_{10})-L-N(R_{10}) CO-CH_2- ; wherein R_9, R_{10} and L are as defined in claim 4, and

the remaining substituents are as defined in claim 4.

6. A process according to claim 4, wherein the spiropyran is a compound of the formula I wherein

Y is 

,

R_1 is C_1-C_6alkoxy, R_2 is hydrogen,

R_3 is NO_2,

R_4 is hydrogen,

R_5 is hydrogen or C_1-C_6alkoxy,

R_6 is hydrogen,

R_7 is hydrogen,

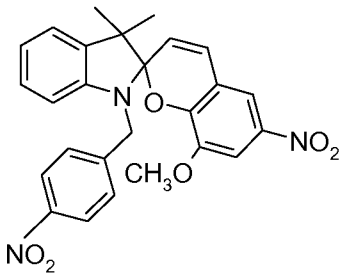
R_a is methyl,

R_b is methyl,

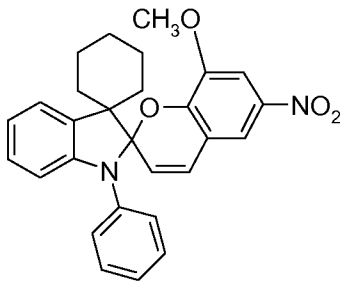
R_{100} is NO_2, bromine, fluorine or CF_3,

R_{200} is hydrogen or fluorine.

7. A process according to claim 4, wherein the spiropyran is a compound of the formula



or



8. A process according to claim 4, wherein the spiropyran is a compound of the formula I wherein

Y is $-CH_2$-COR

R_1 is C_1-C_6alkoxy or C_1-C_6alkylthio

R is $-C_1$-C_6alkoxy or -NHR_9 wherein R_9 is phenyl, phenyl once or more than once substituted by halogen, -CF_3, C_1-C_6alkyl, -C_1-C_6 alkoxy, -S-phenyl or -CO-phenyl

R_2 is hydrogen,

R_3 is NO_2

R_4 is hydrogen,

R_5 is hydrogen,

R_6 is hydrogen,

R_7 is hydrogen,

R_a is methyl.

R_b is methyl.

9. A photochromic spiropyran in the form of a powder which, after dispersion in a printing ink, has at least the double color strength than known forms of the same spiropyran, said powder being obtainable by

d) carefully heating a photochromic spiropyran until it has melted,

e) cooling the melt to obtain a solidified spiropyran, and

f) crushing the solidified spiropyran to obtain a powder.

10. A spiropyran according to claim 9 having the formula I as defined in any one of claims 4-8.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067825

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/00 C07D491/107 C09K9/02

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)
C09D C07D C09K

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 633 109 A (JENNINGS CAROL A [CA] ET AL) 27 May 1997 (1997-05-27)	1,3-8
X	columns 16-37; examples	2,9,10
A	EP 1 260 560 A (XEROX CORP [US]) 27 November 2002 (2002-11-27)	1,3-8
X	examples	2,9,10

-/--

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

[X] 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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 February 2010	10/03/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ellrich, Klaus

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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