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(54) Title: FLUORESCENT PIGMENT CONCENTRATES (57) Abstract Disclosed are low plate-out fluorescent pigment concentrates comprising: (a) a pigment comprising a polymer selected from polyesters, melamine-formaldehyde resins and triazine-formaldehyde resins and a fluorescent dye, and (b) a copolymer of ethylene and carbon monoxide.		

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FLUORESCENT PIGMENT CONCENTRATESTechnical Field

5 This invention relates to fluorescent pigment concentrates for use in a variety of polymers. The concentrates incorporate a low molecular weight ethylene-carbon monoxide copolymer which provides improved resistance to plate-out.

10 Background of the Invention

Fluorescent pigments or daylight fluorescent pigments have been produced commercially since the late 1940's for use in paints, printing inks, and plastics. US patent literature from 1938 forward describes the
15 preparation and use of various fluorescent pigments. Patton, in his Pigment Handbook, (Volume 1, pp 891-903) describes the chemistry, the production, the properties, the major uses, and some of the limitations of fluorescent pigments. An early advancement in the use
20 of fluorescent colorants for plastics is described in U.S. Patent 2,119,189 in which Widmer taught the use of a resinous molecule as a carrier or suitable medium for fluorescent dyes. Later, Switzer, Kazenas, and others utilized extremely friable organic glass-like compounds
25 as carriers for fluorescent dyes. These glass-like compounds included modified sulphonamide resins, urea-melamines, glyceryl phthalates, polyesters, polyamides, vinyl resins, and silica gels.

U.S. Patent 3,922,232 describes a fluorescent
30 colorant comprising particles of a resinous precondensate colored with a fluorescent dye. The precondensate consists of 0.5 to 2 molecules of a carboxylic acid, ester, or anhydride and one mole of a polyhydroxy compound. It is mentioned that additives,
35 such as polyethylene wax and ethylene-acrylic acid

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copolymers, can be added to the precondensate or to the final colorant. The final colorant is useful for coloring polyethylene.

U.S. Patent 4,911,830 teaches the preparation of fluorescent pigment concentrates by mixing about 5 to 40 wt % fluorescent pigment, 5 to 20 wt % inorganic fillers, 2 to 10% silica gel or precipitated silica, 1 to 10% dispersant comprising at least 2 of (a) oxidized polyethylene wax, (b) unoxidized polyethylene wax, (c) ethylene-acrylic acid copolymers, and (d) bivalent metal salts of (a) or (c) and the remainder an ethylene polymer of substantially higher molecular weight up to 50% by weight. Certain types of fluorescent pigments, especially those useful at elevated temperatures, were not effective using this composition, resulting in excessive plate-out.

Although several advancements have been made in the state of the art for the use of fluorescent pigments to color plastics, most commercial fluorescent pigment concentrates continue to have only limited compatibility with a wide range of plastics. This limited compatibility results in many plate-out problems during the compounding of the concentrates and during the extrusion and molding of fluorescent pigmented products.

The detailed explanation of fluorescents and the chemistry involved is outside the scope of this discussion. However, an excellent description is given by Patton in his Pigment Handbook, Volume 1, pp 891-903. Many daylight fluorescent dyes are based on aromatic structures such as the xanthenes, rhodamines, aminonaphthalimides, perinones, and thioindigos.

Fluorescent dyes usually must be in dilute solution in order to fluoresce. Excessive concentration levels sometimes results in a quenching of the fluorescence due to molecular collisions, reabsorption of emitted light,

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and other interactions. If the dyes are stabilized within a rigid glass-like resin, the undesirable deactivation is greatly reduced. Certain resin matrices are preferred for this immobilization of the dye molecules since these resins not only contribute more intense fluorescence, but also provide greater fade and thermal resistance. An example of this glass-like resin medium is one formed by cocondensing a toluene sulfone amide-formaldehyde within a triazine such as melamine or benzoguanamine.

The use of fluorescent pigments in plastics has been slow to develop because of plate-out problems during pigment compounding and during subsequent extruding and molding operations. Plate-out is the undesirable separation of the pigment from the base plastic and its deposition on screws and other metal processing equipment. This phase separation results from the extreme incompatibility of the fluorescent pigment binder and the plastic to be colored. Another limiting factor in the growth of fluorescent colorants in plastics is the relatively poor heat resistance of the glass-like binders for these pigments. Most commercially available fluorescent pigments can withstand temperatures up to 425°F (218°C) for only a very short time. High shear processing conditions which exist in many plastic compounding operations also adversely affect the color stability of many fluorescent pigments.

Description of the Invention

According to the present invention, there are provided low plate-out fluorescent pigment concentrates comprising:

- (a) a pigment comprising a polymer selected from the group consisting of polyesters,

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melamine-formaldehyde resins and
triazine-formaldehyde resins and a
fluorescent dye, and

- 5 (b) a copolymer of ethylene and carbon
monoxide having a molecular weight
of about 1,000 to about 100,000, the
copolymer containing carbon monoxide
residue in the amount of about 5-30%
by weight and the said copolymer
10 being present in sufficient amount
to disperse the pigment.

The fluorescent pigment can be present in an amount
of about 5 to about 50 wt %, and preferably about 20 to
about 40 wt %, based upon the total weight of the
15 concentrate. They must also be sufficiently heat
stable. Combinations of two or more fluorescent
pigments can be used.

Fluorescent pigments are also referred to as
daylight fluorescent colors. The term pigment by
20 definition is understood to mean pure unextended
inorganic or organic colorants which, unlike dyes, are
insoluble in solvents of all kinds. Daylight
fluorescent colors with few exceptions are really not
true pigments but are instead solid solutions of
25 fluorescent dyes in transparent synthetic resins which
are finely ground to a particle size in the range of 2
to 5 microns. These pigments could alternatively be
described as transparent plastic materials, colored with
fluorescent dyes. They contain fluorescent dyes of the
30 type, for example, 4-amino-naphthalimide (yellow) or
rhodamine (red-blue/red) singly or blended together.
There are no genuine blue or green fluorescent dyes; for
these, phthalocyanine pigments combined with optical
brighteners or with yellow fluorescent dyes are
35 employed, yielding shades which, though clearly more

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brilliant than those obtained with normal pigments, do not however attain the luminosity of other fluorescent pigments.

The fluorescent pigments can be said to be
5 fluorescent dyes in molecular solution in the carrier resin.

Examples of fluorescent dyes useful in preparing the fluorescent pigments are the fluorescent brighteners containing sulfo groups, in particular stilbene
10 fluorescent brighteners, especially those of the type of the bis-triazinylaminostilbenedisulfonic acids, the bis-styrylbiphenyls, the bis-styrylbenzenes and the bis-triazolylstilbenedisulfonic acids. The fluorescent brighteners containing sulfonic acid groups can be in
15 the form of their metal salts, for example, lithium, potassium, magnesium or sodium salts, and also ammonium, amine or alkanolamine salts. Fluorescent brightener compounds which have been partially acidified or fluorescent brighteners in the form of the free acid can
20 be used. Any of the fluorescent brighteners containing sulfo groups of U.S. Patent No. 4,466,900 can be used, which is incorporated herein by reference.

Other examples of fluorescent dyes which can be used to prepare the fluorescent pigments are the
25 fluorescent naphthalimide dyes for example, Morton Fluorescent Yellow G (Color Index 75), Fluorol 7GA (Color Index-Fluorescent brightening agent 75), Calcofluor Yellow (Color Index-Fluorescent brightening agent No. 4) and Azosol Brilliant Yellow 6 GF (Color
30 Index-Solvent Yellow 44), and the fluorescent coumarin dyes, for example, Calcofluor White RW (Color Index-Fluorescent brightening agent 68) and Blancophor White AW (Color Index-Fluorescent brightening agent 68). Other useful fluorescent dyes include Rhodanine B,
35 Rhodanine 6 GDN, Auramine, Eosine G, Calcofluor

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White ST, Pontamine White RT, Pontamine White BTS,
Rhodamine Bx, Phthalocyanine, Alkali Blue G,
Phthalocyanine, Rhodamine 7G, Rhodamine FB, Rhodamine S,
Rhodamine 5G, Bright Yellow 3G, Tetramethyl Rhodamine,
5 Rhodamine FG, Rhodamine F4G, Fanal Pink D, Fanal
Violet D, Flexo Yellow 110, Lumogen Yellow D, Fluorol
Green Gold, Fluorol Yellow and Thermoplast F-Orange.

The fluorescent pigments can be prepared with the
aid of dyeing assistants.

10 In contrast to normal pigments, the fastness to
light of fluorescent pigments is only moderate. This is
a result of the poor light fastness of the fluorescent
colorants they contain; the carrier resins themselves
being very stable to light. The addition of UV
15 stabilizers, e.g., benzophenone and benzotriazole
classes, gives marked improvements. Such products are
frequently already present in the fluorescent pigments.

Many of the commercially available fluorescent
pigments recommended for plastics are heat-stable only
20 up to moderate temperatures because of the limited
thermal stability of the carrier resins. These
temperatures for short dwell times range between 180°
and 230°C according to the type of carrier resin and its
degree of 60 cross-linking. Processing temperatures in
25 such range suffice for the final plastic products where
they are molded at a temperature of up to 425°F (218°C),
and preferably 400°F (205°C) or less.

The fluorescent pigments must not be subjected to
too high of shear in the dryblending operation as it may
30 adversely effect the color characteristics of the
fluorescent pigments.

Ethylene-carbon monoxide copolymers useful in the
practice of the present invention are well known in the
art. Such copolymers are typically prepared by the
35 peroxide or gamma-ray irradiation initiated

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copolymerization of ethylene with carbon monoxide. Numerous publications have appeared detailing the synthesis of ethylene-carbon monoxide copolymers. See, for example, U.S. 2,396,963, U.S. 2,436,269, U.S. 2,441,082, U.S. 2,457,271, U.S. 2,495,282, U.S. 2,495,285, U.S. 2,495,286, U.S. 2,526,637, U.S. 2,566,268, U.S. 2,579,033, U.S. 2,595,400, U.S. 2,599,501, U.S. 2,620,325, U.S. 2,634,254, U.S. 2,682,525 and U.S. 2,682,524, each of which is hereby incorporated by reference herein relating to the peroxide initiated polymerization of ethylene and carbon monoxide. See also U.S. 3,083,184, U.S. 3,530,109, U.S. 3,689,460, U.S. 3,694,412, U.S. 3,835,123, U.S. 3,948,873, U.S. 3,984,388, U.S. 4,024,325, U.S. 4,024,326 and U.S. 4,143,096, each of which is hereby incorporated by reference herein, relating to more recently developed methods for the preparation of ethylene-carbon monoxide copolymers.

The carbon monoxide content of ethylene-carbon monoxide copolymers contemplated for use in the practice of the present invention can vary widely. Typically, the carbon monoxide content, based on the weight of the ethylene-carbon monoxide copolymer component of the invention composition, will fall within the range of about 5 up to 50 wt %. Preferred ethylene-carbon monoxide copolymers contain in the range of about 5 up to 35 wt % carbon monoxide.

Low molecular weight ethylene-carbon monoxide copolymers contemplated for use in the practice of the present invention typically have melt viscosities in the range of about 50 up to about 20,000 centipoise at 150°C. Higher molecular weight ethylene-carbon monoxide copolymers contemplated for use in this invention are materials having a melt index in the range of about 0.2 up to 100 g/10 min at 190°C. The most preferred

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molecular weight for the ethylene-carbon monoxide copolymer component depends on the particular application contemplated for the finished article.

5 The process for preparing the low plate-out fluorescent pigment concentrate involves:

(I) dry blending the pigment and polyolefin, preferably using high intensity mixing conditions, but not
10 subjecting the pigment particle surfaces to such high shear so as to materially effect the color characteristics of the pigment particles; and

(II) melt mixing the dry blended mixture
15 at a temperature of 425°F (218°C) or lower and optionally forming the melt-mixed material into a form useful for fabrication. Preferably the forming of the melt-mixed
20 material involves the steps of:

- (a) forming the melt-mixed materials into strands;
- (b) cooling the strands; and
- (c) pelletizing the strands.

25 The temperature during extrusion should not exceed 425°F (218°C).

In formulating the concentrate the ingredients are preferably in powder form and are in dry form.

30 The fluorescent pigment concentrates are dispersed in polymers in order to form molded articles containing fluorescent pigments. Any conventional dispersion or incorporation means, such as, a mixer, can be used.

The dispersions of polymer and fluorescent pigment concentrate are molded, using any conventional molder,
35 into molded articles.

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Generally, sufficient concentrate should be used to provide a concentration of from about 0.10 to about 2 wt % (based on the total weight of the final plastic product) of fluorescent pigment in the final plastic product.

The compositions used to form the final polymer products can contain the usual additives, such as, heat and/or light stabilizers. Some material which act as lubricants may adversely effect the plate-out characteristics.

Example

Basic Formulation:

15	Polyethylene Resin	0-46%
	Fluorescent Pigment	35%
	Filler (equal to or less	10%
	than two microns average	
20	particle size)	
	TiO ₂	2%
	Silcron G-100	2%
	Wax Dispersant	5-51%

25 Note: Inorganic material like barium sulfate or various clays.

Mixing Procedure:

- 30 1. Weigh-out ingredients into high-intensity mixer
2. Mix on medium speed for 1 minute
3. Discharge material

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Extrusion Procedure:

1. Set temperatures no higher than 425°F (218°C)
2. Extrude into strands
- 5 3. Run strands through water bath to cool
4. Run cooled strands through a pelletizer

Plate-Out Test:

- 10 1. Place 5.0 g of concentrate onto polished press plates
2. Put plates into press set at no more than 375°F
3. Apply enough pressure to get a press-out of about 20 mils
- 15 4. Remove plates and cool in water bath
5. Remove pressed material and visually evaluate residue deposited onto plate
6. Rating system:
 - 1 - Excellent (no plate-out)
 - 20 2 - Good (very little plate-out)
 - 3 - Moderate plate-out
 - 4 - Bad plate-out
 - 5 - Very bad plate-out

25 The concentrates rating as OK in this work are rated no higher than a two. A rating of 3 is marginal, and ratings of 4 and 5 are considered to be unacceptable. All others are considered to have too much plate-out.

30

Example 1

Four hundred grams of a low molecular weight polyethylene wax (2,000 molecular weight, 0.920 density) was melted and held in a glass beaker at 250°F (121°C).

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One hundred grams of fluorescent green pigment (Radiant K-6GR6031) was added to the molten polyethylene wax and mixed thoroughly for five minutes using a Cowles mixer at 1800 rpm. After mixing, the molten composition was poured from the beaker onto a cool flat surface and cooled to room temperature. The resulting blend was examined visually for phase separation and compatibility. Compositions which appeared to be compatible were further let down into extrusion grade polypropylene (MFR 12, 0.90 density) at a let-down ratio of 24-parts polypropylene to 1-part pigment master batch and then extruded into 2-mil thick film. The resulting film was examined and rated for pigment dispersion.

15 Example 2

A composition similar to Example 1, except the low molecular weight wax is an oxidized polyethylene (2,000 molecular weight, 0.939 density, and 16 acid number).

20 Example 3

A composition similar to Example 1, except the low molecular weight wax is a polyethylene grafted with maleic anhydride (4,000 molecular weight, 0.908 density, 2-3 acid number).

25

Example 4

A composition similar to Example 1, except the low molecular weight wax is a polypropylene grafted with maleic anhydride (4,000 molecular weight, 0.934 density, 45 acid number).

30

Example 5

A composition similar to Example 1, except that the low molecular weight wax is an ethylene-carbon monoxide

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(E-CO) - copolymer (CO content 2.2%, 2,000 molecular weight, 1.0 density).

Example 6

5 A composition similar to Example 1, except that the low molecular weight wax is an ethylene-carbon monoxide copolymer (CO content 8%, 2,000 molecular weight, 0.96 density).

10 Example 7

 A composition similar to Example 1, except that the low molecular weight wax is an ethylene-carbon monoxide copolymer (CO content 14%, 0.96 density, 3,000 molecular weight).

15

Example 8

 A composition similar to Example 1, except that the low molecular weight wax is a ethylene-carbon monoxide copolymer (CO content 21%, 1.0 density, 2,000 molecular weight).

20

Example 9

 A composition similar to Example 1, except that the low molecular weight wax is an ethylene-carbon monoxide copolymer (CO content 31%, 1500 molecular weight, 1.02 density).

25

 In examples 1 through 4, the low molecular weight dispersant waxes were: an unmodified polyethylene, an oxidized polyethylene, a maleated polyethylene, and a maleated polypropylene respectively. All gave incompatible blends with the fluorescent pigment as evidenced by phase separation in the melt. In Examples 5 and 6, the low molecular weight dispersant waxes were ECO copolymers with about 2% and 8% CO

30

35

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content. Both gave incompatible compositions which phase separated in the melt (see Table 1).

Examples 7 through 9 contained ethylene-carbon monoxide copolymers with 14, 21, and 30% CO content respectively. The compositions were compatible and did not phase separate in the melt nor when cooled to room temperature (see Table 1).

Compositions from Examples 1, 5, 6, 7, 8, and 9 were let down into plastic grade polypropylene homopolymer (MFR 12, density 0.91) at a let down ratio of 24-parts polypropylene to 1-part fluorescent concentrate. The resulting blends were extruded into 2-mil film and examined for pigment dispersion and plate-out problems. As indicated in Table 2, film containing wax dispersants from Examples 1, 5, and 6 exhibited only fair to poor pigment dispersion and considerable plate-out problems. Conversely, film containing ethylene-carbon monoxide wax dispersants with CO levels greater than 8% (Examples 7-9) exhibited excellent pigment dispersion with no evidence of plate-out.

As indicated in Table 3, the low molecular weight ethylene-carbon monoxide copolymers offers superior compatibilities with a wide variety of polymers and resins compared to other low molecular weight polyolefin dispersants commonly used in pigment concentrates.

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TABLE 1

Compatibilities of Low Molecular Weight
Polyolefins with Fluorescent Pigments*

<u>Polyolefin**</u>	<u>Compatibility</u> <u>Polyolefin/Pigment Ratio, (4/1)</u> <u>Green</u>	
Ex. 1 Epolene (trademark) N-14 wax		I
Ex. 2 Epolene E-14 wax		I
Ex. 3 Epolene C-16 wax		I
Ex. 4 Epolene E-43 wax		I
Ex. 5 E-CO (2.2% CO) copolymer wax		I
Ex. 6 E-CO (8% CO) copolymer wax		I
Ex. 7 E-CO (14% CO) copolymer wax		C
Ex. 8 E-CO (21% CO) copolymer wax		C
Ex. 9 E-CO (30% CO) copolymer wax		C

*Radiant K6GR6031

**Low molecular weight polyolefins (1000 to 10,000
molecular weight).

I - incompatible

C - compatible

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TABLE 2

Polypropylene Film
Blends, Parts by Weight

<u>Materials</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Example 1 Concentrate	1					
Example 5 Concentrate		1				
Example 6 Concentrate			1			
Example 7 Concentrate				1		
Example 8 Concentrate					1	
Example 9 Concentrate						1
Polypropylene (12 MFR 0.91 density)	24	24	24	24	24	24
<u>Film Properties</u>						
Pigment Dispersion	Poor	Poor	Fair	Exc	Exc	Exc
Plate Out	Severe	Moderate	Slight	None	None	None

TABLE 3

Compatibilities of E-CO Copolymers
With Various Resins and Polymers

Resins/Polymers	E-CO Copolymer (8% CO)										E-CO Copolymer (21% CO)										ECO Copolymer (30% CO)									
	Epolene C-15																													
Ratio, Polymer/ECO	3:1	1:1	1:3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3	3/1	1/1	1/3
CAB 551-0.02	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Epolene C-15	-	-	-	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Paraffin Wax	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
E-VA - (18% VA)	I	I	CH	C	C	C	C	C	C	CH	I	CH	I	I	CH	I	I	CH	I	I	I	I	I	I	I	I	I	I	I	I
E-VA - (28% VA)	I	I	I	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
AC 540	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Kristalex (trademark) 1120 polystyrene	I	I	I	I	I	I	I	I	I	I	I	I	CH	CH	CH	I	I	CH	I	I	I	I	I	I	I	I	I	I	I	I
Carbowax (trademark) 4000 polyethylene glycol	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Myvaplex (trademark) 600P monoglyceride	I	I	I	I	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Polybutene	I	I	I	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Super Beckacite (trademark) 2000 terpene phenolic	I	I	I	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH
Versamid (trademark) V930 polyamide	I	I	I	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C

I - Incompatible

C - Compatible

CH - Compatible, Hazy

E - VA (Ethylene-Vinyl Acetate)

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The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and
5 scope of the invention.

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CLAIMS

1. A low plate-out fluorescent pigment concentrate characterized as being a blend of:
 - 5 (a) a pigment comprising a polymer selected from the group consisting of polyesters, melamine-formaldehyde resins and triazine-formaldehyde resins and a fluorescent dye, and
 - 10 (b) a copolymer of ethylene and carbon monoxide having a molecular weight of about 1,000 to about 100,000, said copolymer containing carbon monoxide residue in the amount of about 5-30% by weight, said copolymer being present
 - 15 in sufficient amount to disperse said pigment.
2. A concentrate according to Claim 1 wherein said pigment and said polyolefin are each present in an amount of about 5-50% by weight based on the weight
- 20 of the concentrate.
3. A concentrate according to Claim 1 which contains, in addition, up to about 50% by weight of a compatible thermoplastic polymer as a carrier, said
- 25 thermoplastic polymer having a molecular weight of about 10,000 to 100,000.
4. A concentrate according to Claim 3 wherein said thermoplastic polymer is selected from the group
- 30 consisting of polyethylene, polypropylene, polystyrene, polystyrene copolymers and terpolymers, and polyamides.

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5. Process for preparing a low plate-out fluorescent pigment concentrate characterized by dry blending
- (a) a pigment comprising a polymer selected from the group consisting of polyesters, melamine-formaldehyde resins and triazine-formaldehyde resins and a fluorescent dye, and
- (b) a copolymer of ethylene and carbon monoxide having a molecular weight of about 1,000 to about 100,000, said copolymer containing carbon monoxide residue in the amount of about 5-30% by weight, said copolymer being present in sufficient amount to disperse said pigment, said process comprising dry blending said pigment and said polyolefin, melt blending said pigment and said polyolefin at a temperature of about 300°F (149°C) to about 425°F (218°C), and optionally forming the melt-mixed material into a form useful for fabrication.

INTERNATIONAL SEARCH REPORT

PCT/US 92/09378

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09B67/20; C09K11/06; C08K5/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09B ; C09K ; C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB,A,1 341 602 (BASF AG) 25 December 1973 see page 1, line 1 - page 2, line 30 see page 3, line 15 - line 19 ---	1-5
A	US,A,4 911 830 (BROMLEY ET. AL.) 27 March 1990 cited in the application see the whole document ---	1-5
A	US,A,2 119 189 (G. WIDMER) 31 May 1938 cited in the application see the whole document ---	1-5
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 MARCH 1993	02.04.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	KETTERER M.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	
A	FR,A,2 252 387 (SOCIÉTÉ "HERCULES INCORPORATED") 20 June 1975 see page 1, line 1 - page 5, line 3 see page 6, line 25 - page 7, line 14 & US,A,3 922 232 cited in the application ---	1-5
A	US,A,2 938 873 (Z. KAZENAS) 31 May 1960 see column 1, line 1 - column 4, line 34 see column 8, line 27 - line 54 ---	1
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 15/03/93

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