



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : G03G 9/135	A1	(11) International Publication Number: WO 92/14191 (43) International Publication Date: 20 August 1992 (20.08.92)
(21) International Application Number: PCT/NL92/00013 (22) International Filing Date: 21 January 1992 (21.01.92) (30) Priority data: 650,018 4 February 1991 (04.02.91) US (71) Applicant: SPECTRUM SCIENCES B.V. [NL/NL]; Zijdweg 6, NL-2244 BG Wassenaar (NL). (72) Inventors: ALMOG, Yaacov ; 2 Hachalutz Street, 76 251 Rehovot (IL). AVADIK, Frida ; 27 Berenstein Street, 75 503 Rishon Lezion (IL). (74) Agents: DE BRUIJN, Leendert, C. et al.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LIQUID DEVELOPER IMAGING SYSTEM (57) Abstract Liquid toner compositions for electrostatic imaging, which comprise colorant particles, a carrier liquid, at least one charge priming agent selected from alkoxides of aluminum and alkoxides of zirconium reacted with said particles and at least one charge director, wherein said charge priming agent is present in the colorant particles only near the surface thereof.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

- 1 -

1 **LIQUID DEVELOPER IMAGING SYSTEM**2 FIELD OF THE INVENTION

3 This invention relates to the field of electrostatic
4 imaging and, more particularly, to liquid toners containing
5 charge directors and charge priming agents.

6 BACKGROUND OF THE INVENTION

7 In the art of electrostatic photocopying or photo-
8 printing, a latent electrostatic image is generally produced
9 by first providing a photoconductive imaging surface with a
10 uniform electrostatic charge, e.g. by exposing the imaging
11 surface to a charge corona. The uniform electrostatic charge
12 is then selectively discharged by exposing it to a modulated
13 beam of light corresponding, e.g., to an optical image of an
14 original to be copied, thereby forming an electrostatic
15 charge pattern on the photoconductive imaging surface, i.e.
16 a latent electrostatic image. Depending on the nature of the
17 photoconductive surface, the latent image may have either a
18 positive charge (e.g. on a selenium photoconductor) or a
19 negative charge (e.g. on a cadmium sulfide photoconductor).
20 The latent electrostatic image can then be developed by
21 applying to it oppositely charged pigmented toner particles,
22 which adhere to the undischarged "print" portions of the
23 photoconductive surface to form a toner image which is
24 subsequently transferred by various techniques to a copy
25 sheet (e.g. paper).

26 It will be understood that other methods may be
27 employed to form an electrostatic image, such as, for
28 example, providing a carrier with a dielectric surface and
29 transferring a preformed electrostatic charge to the
30 surface. The charge may be formed from an array of styluses.
31 This invention will be described in respect of office
32 copiers, though it is to be understood that it is applicable
33 to other uses involving electrography.

34 In liquid-developed electrostatic imaging, the toner
35 particles are generally dispersed in an insulating non-polar
36 liquid carrier, generally an aliphatic hydrocarbon fraction,
37 which generally has a high volume resistivity above 10^9 ohm
38 -cm, a dielectric constant below 3.0 and a low vapor
39 pressure (less than 10 torr. at 25°C). The liquid developer

- 2 -

1 system further comprises so-called charge directors, i.e.
2 compounds capable of imparting to the toner particles an
3 electrical charge of the desired polarity and uniform
4 magnitude so that the particles may be electrophoretically
5 deposited on the photoconductive surface to form a toner
6 image.

7 In the course of the process, a thin film of the liquid
8 developer is applied to and covers the entire
9 photoconductive imaging surface. The charged toner particles
10 in the liquid developer film migrate to the oppositely-
11 charged areas forming the "print" portions of the latent
12 electrostatic image, thereby forming the toner image and any
13 liquid developer remaining on the photoconductive surface
14 after this stage of the process is recycled back into the
15 liquid developer reservoir.

16 Charge director molecules play an important role in the
17 above-described developing process in view of their function
18 of controlling the polarity and magnitude of the charge on
19 the toner particles. The choice of a particular charge
20 director for use in a specific liquid developer system, will
21 depend on a comparatively large number of physical
22 characteristics of the charge director compound, inter alia
23 its solubility in the carrier liquid, its chargeability, its
24 high electric field tolerance, its release properties, its
25 time stability, etc. All these characteristics are crucial
26 to achieve high quality imaging, particularly when a large
27 number of impressions are to be produced.

28 A wide range of charge director compounds for use in
29 liquid-developed electrostatic imaging are known from the
30 prior art. Examples of charge director compounds are ionic
31 compounds, particularly metal salts of fatty acids, metal
32 salts of sulfo-succinates, metal salts of oxyphosphates,
33 metal salts of alkyl-benzenesulfonic acid, metal salts of
34 aromatic carboxylic acids or sulphonic acids, as well as
35 zwitterionic and non-ionic compounds, such as
36 polyoxyethyleated alkylamines, lecithin, polyvinyl-
37 pyrrolidone, organic acid esters of polyvalent alcohols,
38 etc.

39 In an attempt to improve the quality of the image

- 3 -

1 formed, particularly when using liquid toners containing
2 charge directors, it has been suggested to use adjuvants in
3 the toner compositions, such as polyhydroxy compounds,
4 aminoalcohols, γ -butyrolactone succinimide, an aromatic
5 hydrocarbon, a metallic soap or a salt of a Group Ia, IIa,
6 or IIIa metal.

7 Thus, for example, in U.S. Patent No. 4,707,429
8 entitled "Metallic Soap as Adjuvant for Electrostatic Liquid
9 Developer", a metallic soap adjuvant was used in a toner
10 composition which contained a nonpolar liquid soluble ionic
11 or zwitterionic charge director compound, while in U.S.
12 Patent No. 4,780,389 entitled "Inorganic Metal Salt as
13 Adjuvant for Negative Liquid Electrostatic Developers", a
14 salt of a Group Ia, IIa, or IIIa metal with specified anions
15 was used as adjuvant in a toner composition which contained
16 a nonpolar liquid soluble ionic or zwitterionic charge
17 director compound which imparts a negative charge to
18 thermoplastic resin particles in the toner. The disclosures
19 in both of these U.S. patents is explicitly incorporated
20 herein by reference.

21 As stated in each of these U.S. patents, even when the
22 prior adjuvants are used in conjunction with charge
23 directors, the images obtained using some toner formulations
24 suffer from one or more of the following disadvantages,
25 namely, low resolution, poor solid area coverage (density),
26 image squash and ghosting.

27 U.S. Patent 4,971,883 to Chan et al. describes a liquid
28 toner in which the toner particles are formed of a material
29 which is the reaction product of a polymeric resin having
30 free carboxyl groups and a metal alkoxide.

31 U.S. Patent 4,144,184 to Takahata et al. describes a
32 liquid toner system in which the charge control agent is
33 formed from a reaction product of one of a group of metal
34 alkoxides and an organic compound and is then added to the
35 dispersion of toner particles in carrier liquid.

36 SUMMARY OF THE INVENTION

37 It is an object of the present invention to provide
38 improved liquid toner compositions containing charge
39 directors and charge priming agents. Other objects of the

- 4 -

1 invention will appear from the description which follows.

2 The present invention accordingly provides for a liquid
3 toner for electrostatic imaging, which comprise colorant
4 particles, a carrier liquid, at least one charge priming
5 agent selected from alkoxides of aluminum and alkoxides of
6 zirconium reacted with said particles and at least one
7 charge director, wherein said charge priming agent, if
8 present in said colorant particles, is present only near the
9 surface of said particles. Alkoxides of other tri-valent
10 metals are believed to be useful in the practice of the
11 invention as well.

12 We have found that the colorant particles in such
13 compositions exhibit excellent time stability of charge,
14 high mobility and give rise to images of very good copy
15 quality.

16 The present invention moreover provides an
17 electrostatic imaging process which comprises the steps of:
18 forming a charged latent electrostatic image on a
19 photoconductive surface; applying to said surface charged
20 toner particles from a toner composition according to the
21 present invention, thereby to form a toner image on said
22 surface; and transferring the resulting toner image to a
23 substrate.

24 For purposes of definition in the present specification
25 and claims, it is to be noted that the term alkoxides is
26 intended to include the unsubstituted alkoxide moiety,
27 saturated cyclic alkoxide (e.g. cycloalkyloxy and
28 cycloalkylakoxy), and the alkoxide moiety which is otherwise
29 substituted by one to three radicals which do not have an
30 adverse effect on the charge priming characteristics of the
31 metal alkoxides.

32 BRIEF DESCRIPTION OF THE DRAWINGS

33 Figs. 1-5 show the effect of varying amounts of a
34 charge priming agent in accordance with the invention, on
35 the mobility of toner particles in different liquid toner
36 compositions.

37 DETAILED DESCRIPTION OF THE INVENTION

38 The thermoplastic resins, insulating non polar carrier
39 liquids, colorant particles and charge directors, which may

- 5 -

1 suitably be used in the toner compositions of the invention
2 are known in the art, for example in the two U.S. patents
3 mentioned above. Illustratively, the insulating non-polar
4 liquid carrier, which should preferably also serve as the
5 solvent for the charge directors, is most suitably an
6 aliphatic hydrocarbon fraction having suitable electrical
7 and other physical properties. Preferred solvents are the
8 series of branched-chain aliphatic hydrocarbons and mixtures
9 thereof, e.g. the isoparaffinic hydrocarbon fractions having
10 a boiling range above about 155°C, which are commercially
11 available under the name Isopar (a trademark of the Exxon
12 Corporation). Other carrier liquids such as NORPARs, mineral
13 oils etc., are also useful in the practice of the invention.

14 The charge priming agents utilized in accordance with
15 the present invention are selected from alkoxides of
16 aluminum and zirconium. Aluminum alkoxides are presently
17 preferred. The alkoxide moieties in the charge priming
18 agents may for example be selected from unsubstituted
19 alkoxide moieties having preferably 1-12 carbon atoms,
20 including, for example, methoxy, ethoxy, propoxy,
21 isopropoxy, butoxy, isobutoxy, pentoxy, hexoxy, heptoxy,
22 octoxy, nonoxy, decoxy, undecoxy and dodecoxy, those having
23 1-6 carbon atoms being particularly preferred. However, as
24 pointed out above, "alkoxide" in the present specification
25 and claims includes saturated cyclic alkoxide (e.g.
26 cycloalkyloxy and cycloalkylalkoxy such as cyclopropoxy,
27 cyclobutoxy, cyclopentoxy, cyclohexoxy, cycloheptoxy and
28 cyclooctoxy, as well as cyclohexylmethoxy and 2-
29 cyclohexylethoxy), as well as the alkoxide moiety which is
30 substituted by one to three radicals which do not have an
31 adverse effect on the charge priming characteristics of the
32 metal alkoxides. Such substituents may be for example,
33 halogen such as chlorine or fluorine, alkoxy such as methoxy
34 or ethoxy, and aryl such as phenyl. Thus, such substituted
35 alkoxide radicals include illustratively, 2-chloroethyl,
36 2,2,2-trifluoroethyl, 2-methoxyethyl, benzyl and 2-
37 phenylethyl.

38 It will be appreciated that the alkoxides useful as
39 charge priming agents in accordance with the present

- 6 -

1 invention contain a multiplicity of alkoxide radicals, and
2 that these radicals in any one aluminum or zirconium
3 alkoxide may be the same as each other, or different from
4 each other.

5 The charge priming agents may be included in the liquid
6 toners by any suitable method, and the methods exemplified
7 herein are to be regarded as illustrative only, and not
8 limitative. In a particular embodiment, the charge priming
9 agent is admixed with the diluted toner and the mixture
10 allowed to equilibrate. In another embodiment, the charge
11 priming agent is ground with toner concentrate. It is
12 presently preferred to add the charge director to the
13 diluted toner which is otherwise ready for use, i.e. after
14 the charge priming agent has been incorporated.

15 The invention will be illustrated by the following non-
16 limiting Examples, in which all "parts" are parts by weight.
17 All ratios or percentages are with respect to the non-
18 volatile portion of the liquid toner and refer to the non-
19 volatile solids portions of the respective materials.

20 The charge director used in all the Examples is
21 prepared as follows.

22 PREPARATION OF CHARGE DIRECTOR

23 A four-necked 2 liter glass reactor fitted with a
24 mechanical stirrer and reflux condenser was charged with 300
25 g. of a solution of 10% lecithin (Fisher) in Isopar H and
26 280 g. of 10% basic barium petronate (Witco) solution in
27 Isopar H. To the resulting solution, heated to 80°C, 6g of
28 1-vinyl-2-pyrrolidone was added, followed by 20 g. of a
29 solution of 6 g. lauroyl peroxide (Aldrich) in Isopar H. The
30 mixture was heated to 95°C, and the reaction was allowed to
31 proceed while stirring for 10 hours in a nitrogen
32 atmosphere.

33 EXAMPLE I - Cyan

34 (a) Ten parts of Elvax II 5720 (E.I. du Pont) and five
35 parts of Isopar L (Exxon) are mixed at low speed in a double
36 jacketed planetary mixer connected to an oil heating unit
37 set at 130°C for one hour. A mixture of 1.75 parts of
38 Helioecht Blue (Bayer) and 5 parts of Isopar L are added to
39 the mix in the double planetary mixer and the whole is mixed

- 7 -

1 for a further hour at high speed. Ten parts of Isopar L,
2 preheated to 110°C, are added, and mixing is continued
3 without heating until the temperature of the mixture drops
4 to 40°C.

5 (b) The product of part (a) is diluted with Isopar L to
6 a non-volatile solids content of 11.5%, and transferred to a
7 Sweco grinder, using 0.5 inch cylindrical alumina media and
8 is ground for 41 hours with water cooling. The final median
9 diameter of the resultant toner particles is 2.3 μm .

10 (c) The toner concentrate from part (b) is diluted to a
11 non-volatile solids content of 1.5%, using Isopar H. 100 g
12 portions of the product are then charged with various
13 amounts of aluminum tri(isopropoxide) ("Al(IP)₃"), obtained
14 from Aldrich) as indicated in Fig. 1. The toner is left to
15 equilibrate for 24 hours, then 50 mg./g. charge director is
16 added. Mobility values for different proportions of Al(IP)₃
17 are shown in Fig. 1. For measurement of mobility, see e.g.
18 "Measurements of the Electrophoretic Mobility of Toner
19 Suspensions", by Niv, Y., et al, 3rd Intl. Congress on
20 Advances in Non-Impact Printing Technologies/SPSE, 24-28
21 August 1986, the disclosure of which is incorporated herein
22 by reference.

23 **EXAMPLE II - Red**

24 (a) Thirty grams of a mixture of 86.5% of Elvax II 5720
25 and 13.5% of pigment red 6300 (E.I. du Pont) are melted
26 together with 70 grams of Isopar L at 130°C until the blend
27 is homogeneous.

28 (b) The product of part (a) is allowed to cool to room
29 temperature and transferred to an 01 attritor (Union
30 Process), together with an additional 100 g. of Isopar L.
31 The mixture is ground using stainless steel balls and water
32 cooling ($\approx 20^\circ\text{C}$) for 22 hours, yielding a concentrate of
33 median particle size 2.0 μm .

34 (c) The toner concentrate from part (b) is diluted to a
35 non-volatile solids content of 1.5%, using Isopar H. 100 g
36 portions of the product are then charged with various
37 amounts of Al(IP)₃ as indicated in Fig. 1. The toner is left
38 to equilibrate for 24 hours, then 50 mg./g. charge director
39 is added. Mobility values for the different proportions of

- 8 -

1 $\text{Al}(\text{IP})_3$ are shown in Fig. 1.

2 **EXAMPLE III - Cyan**

3 (a) Ten parts of Elvax II 5950 (E.I. du Pont) and five
4 parts of Isopar L (Exxon) are mixed at low speed in a
5 jacketed double planetary mixer connected to an oil heating
6 unit set at 130°C for one hour. 5 parts of Isopar L are
7 added to the mix and the whole is mixed for a further hour
8 at high speed. Ten parts of Isopar L, preheated to 110°C,
9 are added, and mixing is continued without heating until the
10 temperature of the mixture drops to 40°C.

11 (b) Ninety grams of the product of part (a) is
12 transferred to an 01 attritor together with 4.35 g. of
13 Pigment cyan BT-583 (Heaubch) and 120 g. Isopar L. The
14 mixture is ground for 22 hours with water cooling ($\approx 20^\circ\text{C}$).
15 The resultant toner particles have a median (weight)
16 diameter of about 1.9 μm .

17 (c) The toner concentrate from part (b) is diluted to a
18 non-volatile solids content of 1.5%, using Isopar H. 100 g
19 portions of the product are then charged with increased
20 amounts of $\text{Al}(\text{IP})_3$, as indicated in Fig. 3. The toner is
21 left to equilibrate for 24 hours, then 50 mg./g. charge
22 director is added. Mobility values for the different
23 proportions of $\text{Al}(\text{IP})_3$ are shown in Fig. 3.

24 **EXAMPLE IV - Black**

25 (a) Ten parts of Elvax II 5950 (E.I. du Pont) and five
26 parts of Isopar L (Exxon) are mixed at low speed in a
27 jacketed double planetary mixer connected to an oil heating
28 unit set at 130°C for one hour. 5 parts of Isopar L are
29 added to the mix and the whole is mixed for a further hour
30 at high speed. Ten parts of Isopar L, preheated to 110°C,
31 are added, and mixing is continued without heating until the
32 temperature of the mixture drops to 40°C.

33 (b) Ninety grams of the product of part (a) is
34 transferred to a 01 attritor together with 7.5 g. of Mogul L
35 (Cabot) and 120 g. Isopar L. The mixture is ground for 24
36 hours with water cooling ($\approx 20^\circ\text{C}$). The resultant toner
37 particles have a median (by weight) diameter of about 2.1
38 μm .

39 (c) The toner concentrate from part (b) is diluted to a

- 9 -

1 non-volatile solids content of 1.5%, using Isopar H. 100 g
2 portions of the product are then charged with various
3 amounts of $\text{Al}(\text{IP})_3$, as indicated in Fig. 3. The toner is
4 left to equilibrate for 24 hours, then 50 mg./g. charge
5 director is added. Mobility values for the different
6 proportions of $\text{Al}(\text{IP})_3$ are shown in Fig. 3.

7 **EXAMPLE V - Magenta**

8 (a) Ten parts of Elvax II 5950 (E.I. du Pont) and five
9 parts of Isopar L (Exxon) are mixed at low speed in a
10 jacketed double planetary mixer connected to an oil heating
11 unit set at 130°C for one hour. 5 parts of Isopar L are
12 added to the mix and the whole is mixed for a further hour
13 at high speed. Ten parts of Isopar L, preheated to 110°C,
14 are added, and mixing is continued without heating until the
15 temperature of the mixture drops to 40°C.

16 (b) Ninety grams of the product of part (a) is
17 transferred to an 01 attritor together with 4.5 g. of
18 Pigment F2B Fine Red (Toyo Ink) and 120 g. Isopar L. The
19 mixture is ground for 22 hours with water cooling ($\approx 20^\circ\text{C}$).
20 The resultant toner particles have a median (by weight)
21 diameter of about 0.8 μm .

22 (c) The toner concentrate from part (b) is diluted to a
23 non-volatile solids content of 1.5%, using Isopar H. 100 g
24 portions of the product are then charged with various
25 amounts of $\text{Al}(\text{IP})_3$, as indicated in Fig. 3. The toner is
26 left to equilibrate for 24 hours, then 50 mg./g. charge
27 director is added. Mobility values for the different
28 proportions of $\text{Al}(\text{IP})_3$ are shown in Fig. 3.

29 **EXAMPLE VI - Cyan**

30 (a) Ten parts of Elvax II 5720 (E.I. du Pont) and five
31 parts of Isopar L (Exxon) are mixed at low speed in a
32 jacketed planetary mixer connected to an oil heating unit
33 set at 130°C for one hour. A mixture of 1.75 parts Helioecht
34 Blue and 5 parts of Isopar L are added to the mix and the
35 whole is mixed for an additional hour at high speed. Ten
36 parts of Isopar L, preheated to 110°C, are added, and mixing
37 is continued without heating until the temperature of the
38 mixture drops to 40°C.

39 (b) The product of part (a) is diluted with Isopar L to

- 10 -

1 a non-volatile solids content of 11.5% and transferred to a
2 Sweco grinder using 0.5 inch cylindrical alumina media and
3 is ground for 41 hours with water cooling. The final median
4 diameter of the resultant toner particles is 2.3 μm .

5 (c) Two hundred grams of the toner concentrate from
6 part (b) is transferred into a Union Process 01 attritor and
7 0.52 g. of $\text{Al}(\text{IP})_3$ is added. The mixture is ground for two
8 hours. It is then diluted to 1.5% non-volatile solids
9 content, after a 24 hour waiting period. 50 mg./g. charge
10 director is added to 100 g. of the above working dispersion.
11 The mobility value is 2.5 on a scale on which the mobility
12 for similar material without added $\text{Al}(\text{IP})_3$ is zero.

13 **EXAMPLE VII - Cyan**

14 When Example VI was repeated, but substituting aluminum
15 tri(isobutoxide) for the $\text{Al}(\text{IP})_3$, similar results are
16 obtained.

17 **EXAMPLE VIII - Cyan**

18 When Example VI was repeated, but substituting aluminum
19 tri(ethoxide) for the $\text{Al}(\text{IP})_3$, similar results are obtained.

20 **EXAMPLE IX - Yellow**

21 (a) Thirty grams of a mixture of 86.5% of Elvax II
22 5650T and 13.5% of Sicomet Yellow D-1350 (BASF) are melted
23 together with 70 grams of Isopar L at 100°C until a
24 homogeneous blend is obtained.

25 (b) The product of part (a) is allowed to cool to room
26 temperature and transferred to an 01 attritor together with
27 an additional 100 g. of Isopar L. The mixture is ground
28 using stainless steel balls and water cooling ($\approx 20^\circ\text{C}$) for 22
29 hours, yielding a concentrate of median particle size of 1.7
30 μm .

31 (c) The toner concentrate from part (b) is diluted to a
32 non-volatile solids content of 1.5%, using Isopar H. 100 g
33 portions of the product are then charged with various
34 amounts of $\text{Al}(\text{IP})_3$ as indicated in Fig. 2. The toner is left
35 to equilibrate for 24 hours, then 50 mg./g. charge director
36 is added. Mobility values for the different proportions of
37 $\text{Al}(\text{IP})_3$ are shown in Fig. 2.

38 **EXAMPLE X - Cyan**

39 (a) Ten parts of Elvax II 5720 (E.I. du Pont) and five

- 11 -

1 parts of Isopar L (Exxon) are mixed at low speed in a
 2 jacketed planetary mixer connected to an oil heating unit
 3 set at 130°C for one hour. A mixture of 1.75 parts Helioecht
 4 Blue and 5 parts of Isopar L are added to the mix and the
 5 whole is mixed for an additional hour at high speed. Ten
 6 parts of Isopar L, preheated to 110°C, are added, and mixing
 7 is continued without heating until the temperature of the
 8 mixture drops to 40°C.

9 (b) The product of part (a) is diluted with Isopar L to
 10 a non-volatile solids content of 11.5% and transferred to a
 11 Sweco grinder using 0.5 inch cylindrical alumina media and
 12 is ground for 22 hours with water cooling ($\approx 20^\circ\text{C}$). The
 13 resultant toner particles have a median diameter of 2.3 μm .

14 (c) 220 g. of the toner concentrate from part (b) is
 15 transferred into an 01 attritor and 0.52 g. of $\text{Al}(\text{IP})_3$ is
 16 added. The mixture is ground for two hours. It is then
 17 diluted with Isopar H to 1.5% non-volatile solids content,
 18 after a 24 hour waiting period. 1.2 kg. of the 1.5%
 19 dispersion is charged with 7 mg./g. charge director and
 20 placed in an 870 Savin photocopier. This copier had been
 21 modified to allow for varying process voltages. The
 22 potential on the photoconductor is regulated to 1400 V and
 23 the potential applied on the transfer corotron is 9 KV. The
 24 copy quality parameters as measured using the Macbeth type
 25 TR 927 reflection densitometer, are summarized in Table 1.

TABLE 1

	Control (no $\text{Al}(\text{IP})_3$)		$\text{Al}(\text{IP})_3$ Treated	
	S.A.D.	T.E.	S.A.D.	T.E.
Savin 2200+	0.36	25%	1.46	88%
Printers Stock	0.85	42%	1.70	84%

35 Where T.E. is the transfer efficiency of image transfer
 36 from the photoconductor to the substrate and S.A.D. is the
 37 solid area density of the transferred image.

EXAMPLE XI - Black

38 (a) Ten parts of Surlyn 1652 (E.I. du Pont) and five

- 12 -

1 parts of Isopar L (Exxon) are mixed at low speed in a
2 jacketed double planetary mixer connected to an oil heating
3 unit set at 130°C for one hour. 5 parts of Isopar L are
4 added to the mix and the whole is mixed for an additional
5 hour at high speed. Ten parts of Isopar L, preheated to
6 110°C, are added, and mixing is continued at high speed for
7 another hour.

8 (b) One hundred grams of the product of part (a) is
9 transferred to an 01 attritor together with 3.9 g. Elftex 12
10 carbon black (Cabot) and 120 g. Isopar L. The mixture is
11 ground for 24 hours using water cooling ($\approx 20^\circ\text{C}$). The
12 resultant toner particles have a median (by weight) diameter
13 of 1.6 μm .

14 (c) The toner concentrate from part (b) is diluted to a
15 non-volatile solids content of 1.5%, using Isopar H. 100 g
16 portions of the product are then charged with various
17 amounts of $\text{Al}(\text{IP})_3$, as shown in Fig. 5. The toner is left to
18 equilibrate for 24 hours, then 50 mg./g. charge director is
19 added. Mobility values for the different proportions of
20 $\text{Al}(\text{IP})_3$ are shown in Fig. 5.

21 **EXAMPLE XII - Black**

22 (a) Ten parts of Surlyn 1652 (E.I. du Pont) and five
23 parts of Isopar L (Exxon) are mixed at low speed in a
24 jacketed double planetary mixer connected to an oil heating
25 unit set at 130°C for one hour. 5 parts of Isopar L are
26 added to the mix and the whole is mixed for an additional
27 hour at high speed. Ten parts of Isopar L, preheated to
28 110°C, are added, and mixing is continued at high speed for
29 another hour.

30 (b) One hundred grams of the product of part (a) is
31 transferred to an 01 attritor together with 3.9 g. Mogul L
32 and 120 g. Isopar L. The mixture is ground for 24 hours
33 using water cooling ($\approx 20^\circ\text{C}$). The resultant toner particles
34 have a median (by weight) diameter of 1.6 μm .

35 (c) The toner concentrate from part (b) is diluted to a
36 non-volatile solids content of 1.5%, using Isopar H. 100 g
37 portions of the product are then charged with various
38 amounts of $\text{Al}(\text{IP})_3$, as shown in Fig. 5. The toner is left to
39 equilibrate for 24 hours, then 50 mg./g. charge director is

- 13 -

1 added. Mobility values for the different proportions of
2 $\text{Al}(\text{IP})_3$ are shown in Fig. 5.

3 **EXAMPLE XIII - Yellow**

4 (a) Ten parts of Surlyn 1652 (E.I. du Pont) and five
5 parts of Isopar L (Exxon) are mixed at low speed in a
6 jacketed planetary mixer connected to an oil heating unit
7 set at 130°C for one hour. 5 parts of Isopar L are added to
8 the mix and the whole is mixed for an additional hour at
9 high speed. Ten parts of Isopar L, preheated to 110°C, are
10 added, and mixing is continued at high speed for another
11 hour. Mixing is continued after removing the heat source,
12 until the temperature of the mixture drops to 40°C.

13 (b) Ninety grams of the product of part (a) is
14 transferred to an 01 attritor together with 3.1 g. Sicomett
15 Yellow D-1350 and 120 g. Isopar L. The mixture is ground for
16 26 hours using water cooling ($\approx 20^\circ\text{C}$). The resultant toner
17 particles have a median (weight) diameter of 0.6 μm .

18 (c) The toner concentrate from part (b) is diluted to a
19 non-volatile solids content of 1.5%, using Isopar H. 100 g
20 portions of the product are then charged with various
21 amounts of $\text{Al}(\text{IP})_3$, as shown in Fig. 4. The toner is left to
22 equilibrate for 24 hours, then 50 mg./g. charge director is
23 added. Mobility values for the different proportions of
24 $\text{Al}(\text{IP})_3$ are shown in Fig. 4.

25 **EXAMPLE XIV - Cyan**

26 (a) Ten parts of Surlyn 1652 (E.I. du Pont) and five
27 parts of Isopar L (Exxon) are mixed at low speed in a
28 jacketed planetary mixer connected to an oil heating unit
29 set at 130°C for one hour. 5 parts of Isopar L are added to
30 the mix and the whole is mixed for an additional hour at
31 high speed. Ten parts of Isopar L, preheated to 110°C, are
32 added, and mixing is continued at high speed for another
33 hour. Mixing is continued after removing the heat source,
34 until the temperature of the mixture drops to 40°C.

35 (b) One hundred grams of the product of part (a) is
36 transferred to an 01 attritor together with 3.45 g. of Cyan
37 BT 583 pigment and 100 g. Isopar L. The mixture is ground
38 for 24 hours using water cooling ($\approx 20^\circ\text{C}$). The resultant
39 toner particles have a median (weight) diameter of 0.8 μm .

- 14 -

1 (c) The toner concentrate from part (b) is diluted to a
2 non-volatile solids content of 1.5%, using Isopar H. 100 g
3 portions of the product are then charged with various
4 amounts of $\text{Al}(\text{IP})_3$, as shown in Fig. 4. The toner is left to
5 equilibrate for 24 hours, then 50 mg./g. charge director is
6 added. Mobility values for the different proportions of
7 $\text{Al}(\text{IP})_3$ are shown in Fig. 4.

8 EXAMPLE XV - Magenta

9 (a) 10 parts of Surlyn 1652 (E.I. du Pont) and 5 parts
10 of Isopar L (Exxon) are mixed at low speed in a jacketed
11 planetary mixer connected to an oil heating unit set at
12 130°C for one hour. 5 parts of Isopar L are added to the mix
13 and the whole is mixed for an additional hour at high speed.
14 Ten parts of Isopar L, preheated to 110°C, are added, and
15 mixing is continued at high speed for another hour. Mixing
16 is continued after removing the heat source, until the
17 temperature of the mixture drops to 40°C.

18 (b) One hundred grams of the product of part (a) is
19 transferred to an 01 attritor together with 3.45 g. of
20 Pigment F2B Fine Red (Toyo Ink) and 100 g. Isopar L. The
21 mixture is ground for 24 hours using water cooling ($\approx 20^\circ\text{C}$).
22 The resultant toner particles have a median (by weight)
23 diameter of 0.7 μm .

24 (c) The toner concentrate from part (b) is diluted to a
25 non-volatile solids content of 1.5%, using Isopar H. 100 g
26 portions of the product are then charged with various
27 amounts of $\text{Al}(\text{IP})_3$, as shown in Fig. 4. The toner is left to
28 equilibrate for 24 hours, then 50 mg./g. charge director is
29 added. Mobility values for the different proportions of
30 $\text{Al}(\text{IP})_3$ are shown in Fig. 4.

31 EXAMPLE XVI

32 (a) Ten parts of Elvax II 5720 (E.I. du Pont) and five
33 parts of Isopar L (Exxon) are mixed at low speed in a
34 jacketed double planetary mixer connected to an oil heating
35 unit set at 130°C for one hour. Five parts of Isopar L are
36 added to the mix and the whole is mixed for an additional
37 hour at high speed. Five parts of Isopar L, preheated to
38 110°C, are added and mixing is continued at high speed for a
39 further hour. The heating unit is then disconnected and

- 15 -

1 mixing is continued until the temperature of the mixture
2 drops to 40°C.

3 (b) A mixture of 750 g. of the product of part (a), 53
4 g. Lionel Red 4576 (Toyo Ink) and 1100 g. of Isopar L, is
5 ground for 24 hours in a Union Process 1S attritor, using
6 stainless steel balls, with water cooling. The final median
7 diameter is 0.7 μ .

8 (c) The concentrate prepared in (b) was diluted to a
9 9.4% non-volatile solids content and 220 g. were transferred
10 to an 01 attritor and ground for 2 hours, using water
11 cooling.

12 (d) The concentrate prepared in (b) was diluted to a
13 9.4% non-volatile solids content and 220 g. were transferred
14 to an 01 attritor, together with 0.206 g. Al(IP)₃, and the
15 mixture ground for 2 hours, using water cooling.

16 (e) The concentrate prepared in (c) was suspended in
17 Isopar L at a dilution of 1.5% non-volatile solid content,
18 and charge director was added in the proportion of 28 mg./g.
19 of toner solids. This developer was tested in an 870 Savin
20 photocopier. This copier had been modified to allow for
21 varying process voltages. The potential on the
22 photoconductor is regulated to 1400 V and the potential
23 applied on the transfer corotron is 9 KV. The copy quality
24 parameters as measured using the Macbeth type TR 927
25 reflection densitometer, are summarized in Table 2
26 ("Control"). This material charges in a bi-polar manner,
27 i.e. some of the particles charge positive and some
28 negative.

29 (f) The concentrate prepared under (d) was treated
30 exactly as described in (e) and gave the results noted in
31 Table 2 ("Al(IP)₃ treated").

TABLE 2

	Control (no Al(IP) ₃)		Al(IP) ₃ Treated	
	S.A.D.	T.E.	S.A.D.	T.E.
Savin 2200+	0.80	74%	1.43	96%
Printers Stock	1.10	86%	1.90	97%

- 16 -

1 -----

2 Where T.E. is the transfer efficiency of image transfer
3 from the photoconductor to the substrate and S.A.D. is the
4 solid area density of the transferred image.

5 While the present invention has been particularly
6 described, persons skilled in the art will appreciate that
7 many variations and modification can be made. Therefore, the
8 invention is not to be construed as restricted to the
9 particularly described embodiments, rather the scope, spirit
10 and concept of the invention will be more readily understood
11 by reference to the claims which follow.

- 17 -

1 CLAIMS

- 2 1. Liquid toner compositions for electrostatic imaging,
3 which comprise colorant particles, a carrier liquid, at
4 least one charge priming agent selected from alkoxides of
5 aluminum and alkoxides of zirconium reacted with said
6 particles and at least one charge director, wherein said
7 charge priming agent, if present in said colorant particles,
8 is present only near the surface of said particles.
- 9
- 10 2. Liquid toner compositions according to claim 1, wherein
11 said colorant particles comprise thermoplastic resin.
- 12
- 13 3. Liquid toner compositions according to claim 1 or claim
14 2, wherein the alkoxide moieties in the alkoxides of the
15 charge priming agent are selected from unsubstituted
16 alkoxide moieties, saturated cyclic alkoxide moieties, and
17 alkoxide moieties which are otherwise substituted by one to
18 three radicals which do not have an adverse effect on the
19 charge priming characteristics of the metal alkoxides,
20 provided that the alkoxide moieties in any metal alkoxide
21 charge priming agent may be the same or different.
- 22
- 23 4. Liquid toner compositions according to claim 3, wherein
24 said unsubstituted alkoxide moieties contain 1-12 carbon
25 atoms.
- 26
- 27 5. Liquid toner compositions according to claim 4, wherein
28 said unsubstituted alkoxide moieties contain 1-6 carbon
29 atoms.
- 30
- 31 6. Liquid toner compositions according to claim 3, wherein
32 said saturated cyclic alkoxide moieties are selected from
33 cycloalkyloxy and cycloalkylalkoxy.
- 34
- 35 7. Liquid toner compositions according to claim 3, wherein
36 the substituents in said otherwise substituted alkoxy
37 moieties are selected from halogen, alkoxy and aryl.
- 38
- 39 8. Liquid toner compositions according to any of the

- 18 -

1 preceding claims, wherein said at least one charge priming
2 agent is incorporated by adding it to such composition and
3 allowing the mixture to come to equilibrium with the carrier
4 liquid and colorant particles before the incorporation of
5 said at least one charge director in said composition.

6

7 9. An electrostatic imaging process which comprises the
8 steps of:

9 forming a latent electrostatic image on a surface;

10 applying to said surface charged colorant particles
11 from a liquid toner composition according to any of the
12 preceding claims, thereby forming a developed toner image on
13 said surface; and

14 transferring the resulting toner image to a substrate.

15

16 10. A process for producing liquid toner compositions for
17 electrostatic imaging, which comprise colorant particles, a
18 carrier liquid and at least one charge director comprising
19 the steps of:

20 forming the colorant particles dispersed in a quantity
21 of the carrier liquid;

22 adding at least one charge priming agent selected from
23 alkoxides of aluminum and alkoxides of zirconium to said
24 colorant particles dispersed the quantity of carrier liquid;
25 and

26 adding the at least one charge director to the mixture
27 of colorant particles, carrier liquid and charge priming
28 agent.

29

30 11. A process according to claim 10, wherein said colorant
31 particles comprise thermoplastic resin.

32

33 12. A process according to claim 10 or claim 11, wherein the
34 alkoxide moieties in said metal alkoxides are selected from
35 unsubstituted alkoxide moieties, saturated cyclic alkoxide
36 moieties, and alkoxide moieties which are otherwise
37 substituted by one to three radicals which do not have an
38 adverse effect on the charge priming characteristics of the
39 metal alkoxides, provided that the alkoxide moieties in any

- 19 -

1 metal alkoxide charge priming agent may be the same or
2 different.

3

4 13. Liquid toner compositions according to claim 12, wherein
5 said unsubstituted alkoxide moieties contain 1-12 carbon
6 atoms.

7

8 14. Liquid toner compositions according to claim 13, wherein
9 said unsubstituted alkoxide moieties contain 1-6 carbon
10 atoms.

11

12 15. Liquid toner compositions according to claim 12, wherein
13 said saturated cyclic alkoxide moieties are selected from
14 cycloalkyloxy and cycloalkylalkoxy.

15

16 16. Liquid toner compositions according to claim 12, wherein
17 the substituents in said otherwise substituted alkoxy
18 moieties are selected from halogen, alkoxy and aryl.

19

20 17. Liquid toner compositions according to any of claims 10-
21 16, wherein said at least one charge priming agent is
22 incorporated by adding it to such composition and allowing
23 the mixture to come to equilibrium with the carrier liquid
24 and colorant particles before the incorporation of said at
25 least one charge director in said

1/5

Fig.1

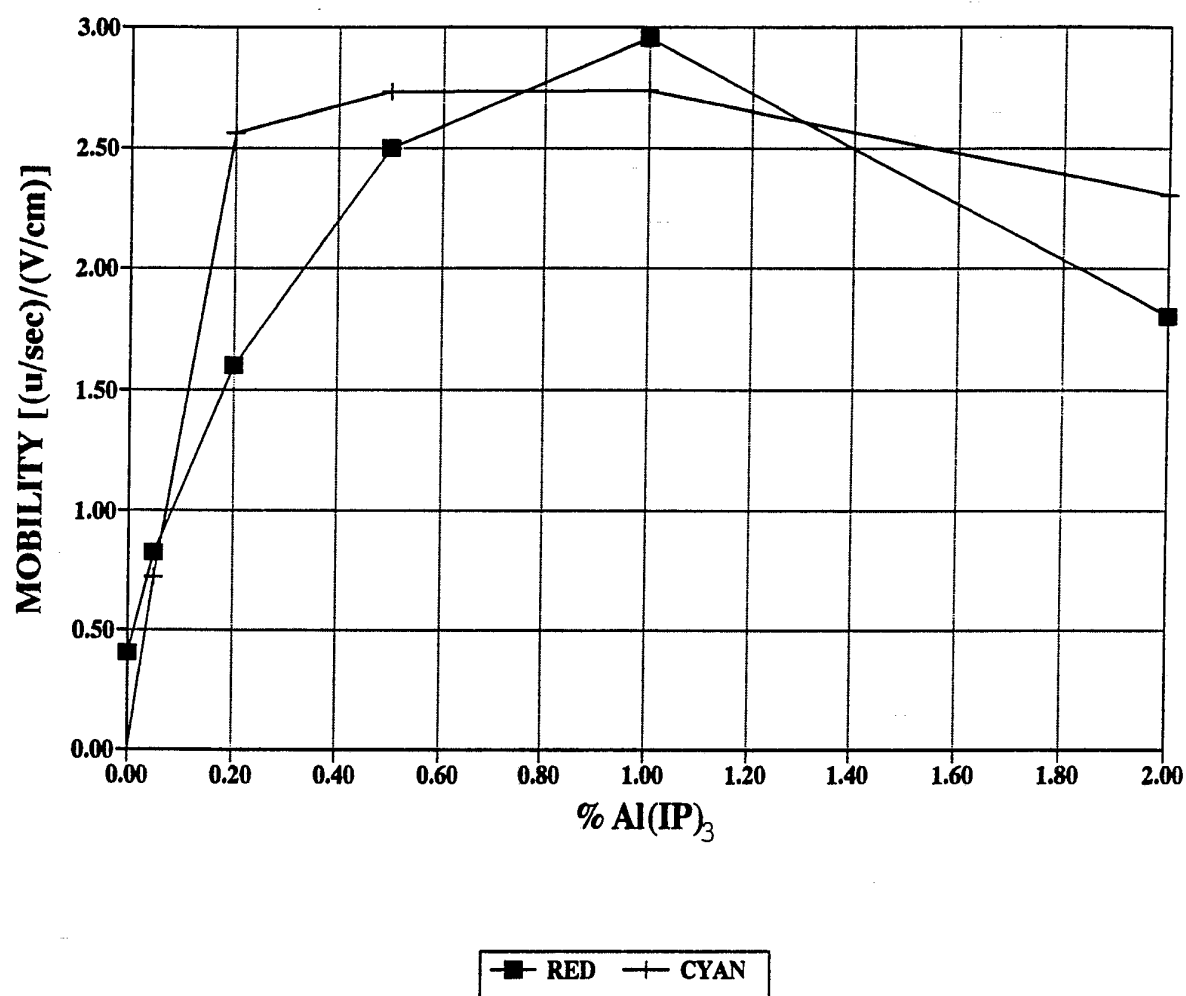
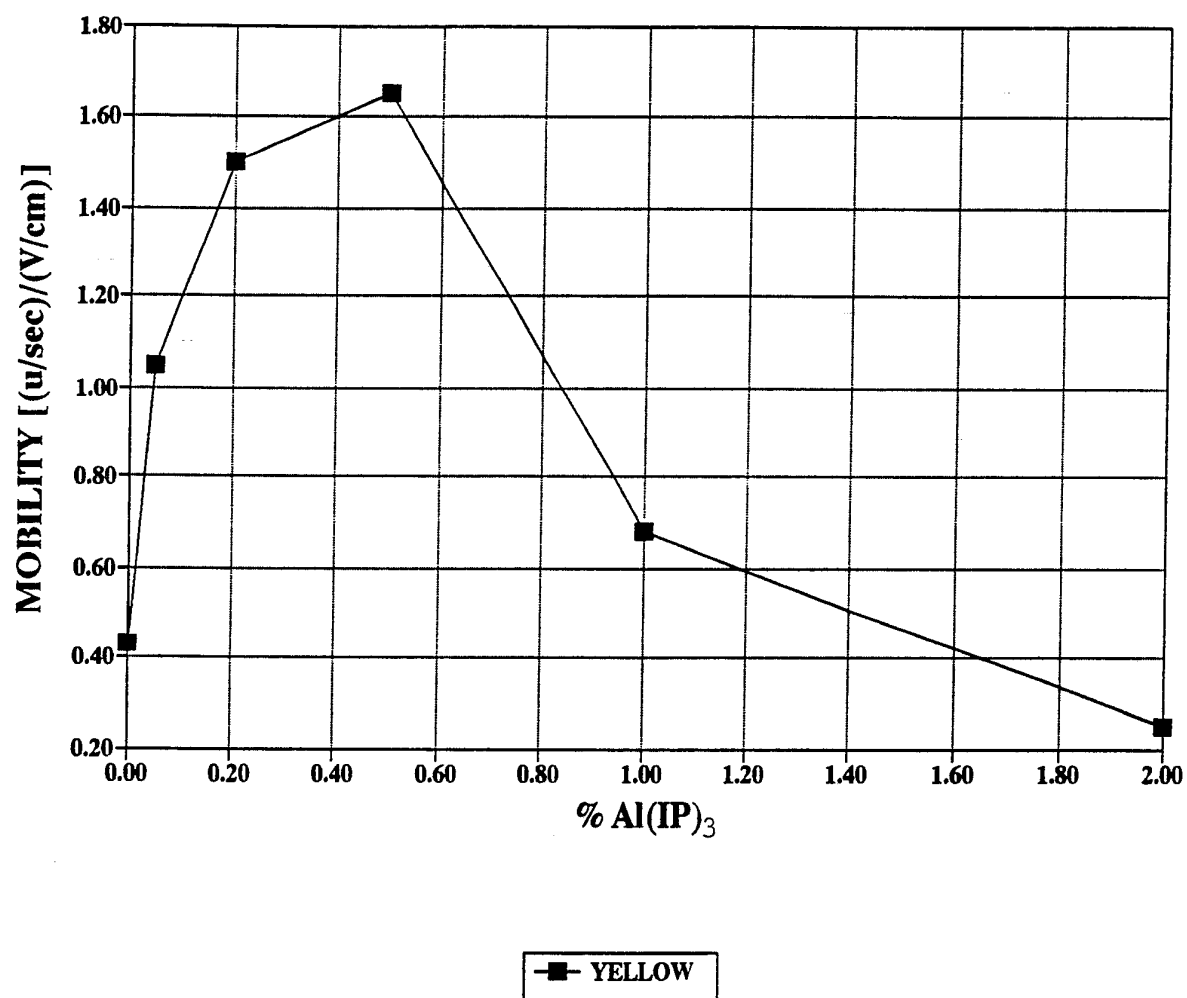


Fig.2



3/5

Fig.3

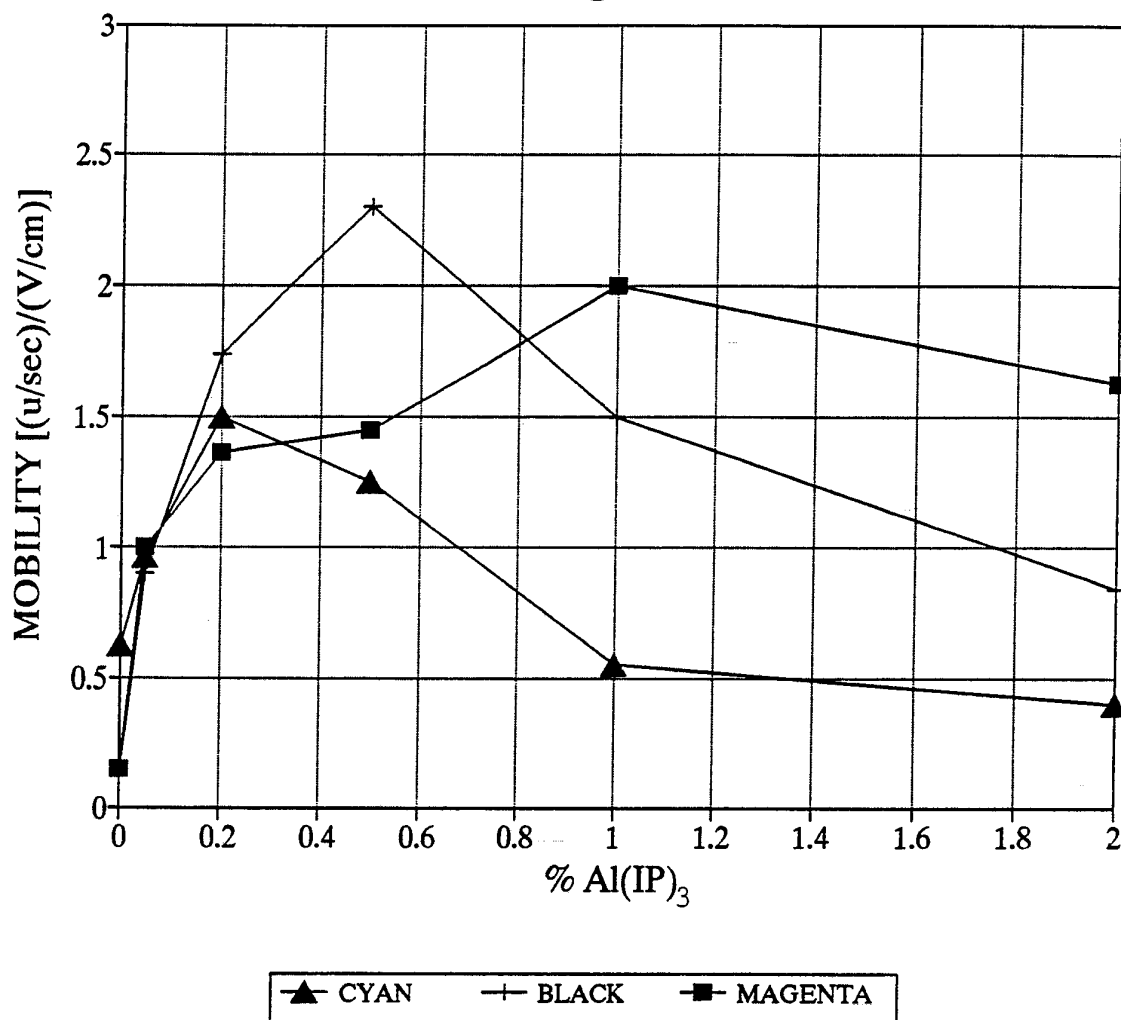


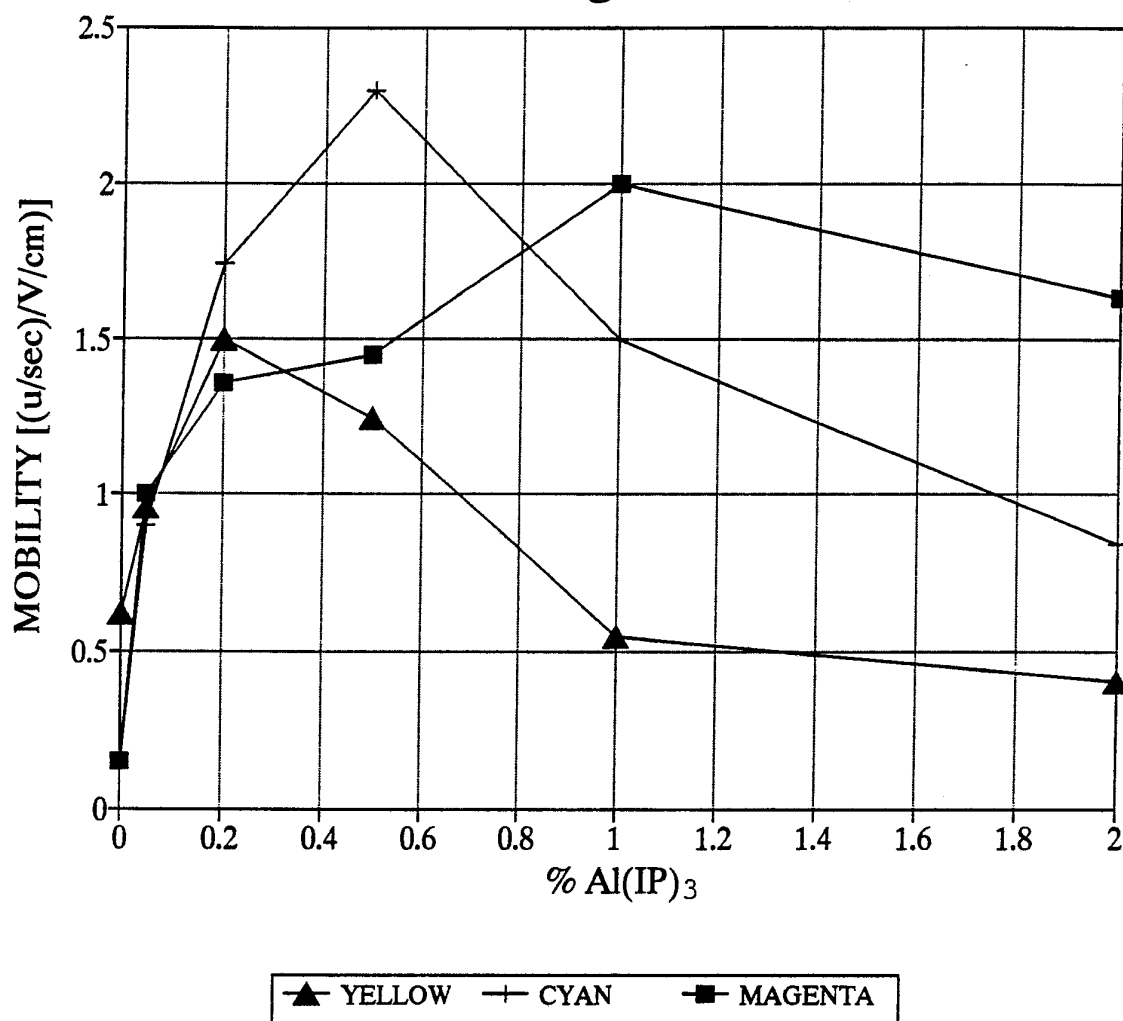
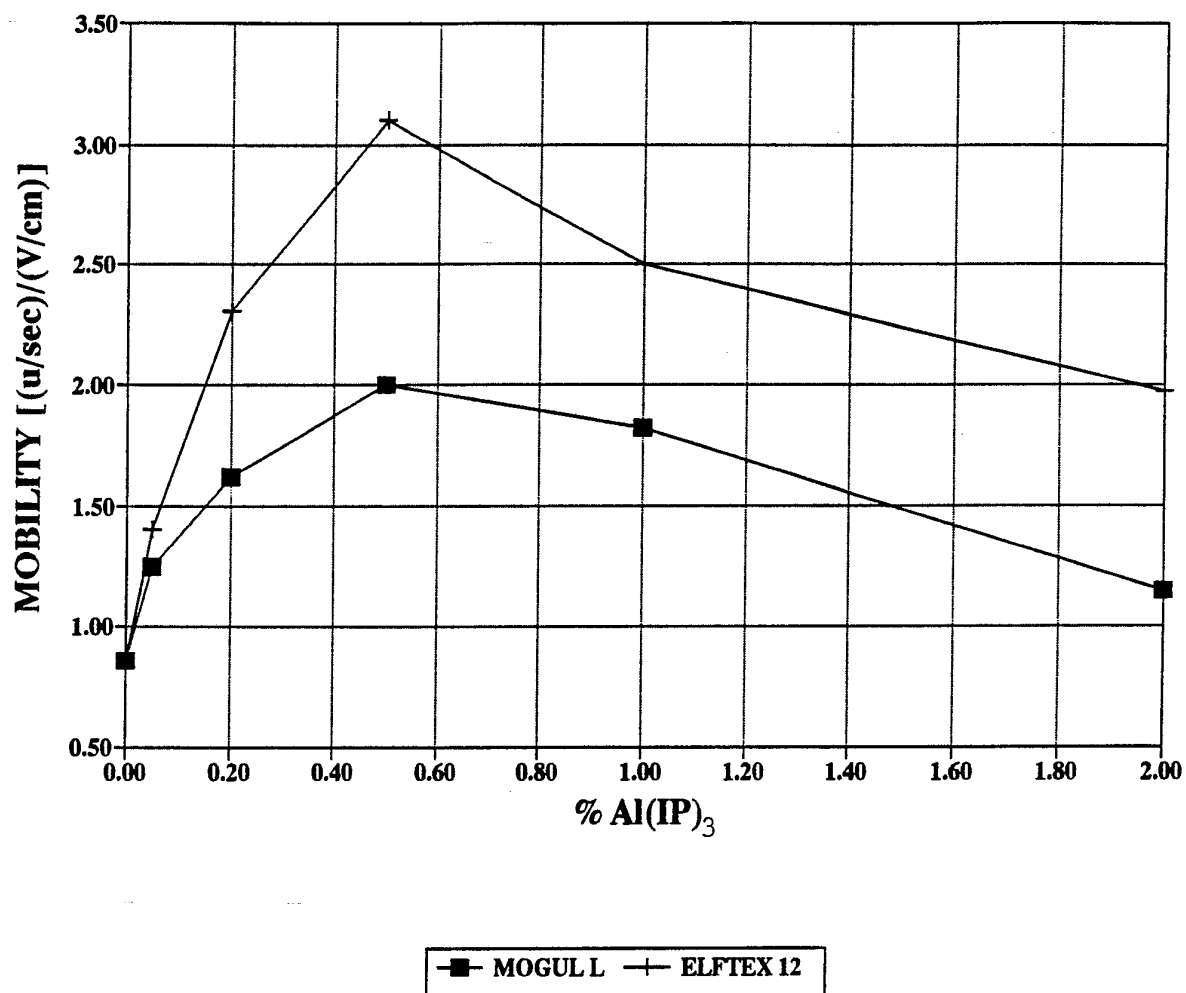
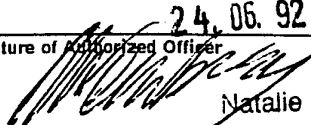
Fig.4

Fig.5



INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 92/00013

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 IPC5: G 03 G 9/135						
II. FIELDS SEARCHED Minimum Documentation Searched⁷ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: bottom; border-right: 1px solid black;">IPC5</td> <td>G 03 G</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸			Classification System	Classification Symbols	IPC5	G 03 G
Classification System	Classification Symbols					
IPC5	G 03 G					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹						
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
P,X	EP, A1, 0436176 (DXIMAGING) 10 July 1991, see page 2 - page 5; claims 1,2 --	1,2,9- 11				
A	EP, A2, 0373776 (MINNESOTA MINING AND MANUFACTURING COMPANY) 20 June 1990, see the whole document --	1-17				
A	US, A, 4971883 (DOMINIC M. CHAN ET AL) 20 November 1990, see the whole document --	1-17				
A	US, A, 4275136 (SADAO MURASAWA ET AL) 23 June 1981, see the whole document --	1-17				
* Special categories of cited documents: ¹⁰ "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 "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						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search 8th May 1992	Date of Mailing of this International Search Report 24.06.92					
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer  Natalie Weinberg					

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4144184 (KEI TAKAHATA ET AL) 13 March 1979, see the whole document -- -----	1-17

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/NL 92/00013**

SA 56345

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/03/92. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0436176	10/07/91	AU-B- 616129	17/10/91
		AU-D- 6830790	01/08/91
		CN-A- 1053848	14/08/91
		US-A- 4994341	19/02/91
EP-A2- 0373776	20/06/90	CA-A- 2003560	13/06/90
		JP-A- 2201481	09/08/90
		US-A- 4892798	09/01/90
		US-A- 4985321	15/01/91
US-A- 4971883	20/11/90	AU-B- 618689	02/01/92
		AU-D- 6308290	01/08/91
		CA-A- 2025948	26/03/91
		CN-A- 1051093	01/05/91
		EP-A- 0420083	03/04/91
		JP-A- 3179366	05/08/91
US-A- 4275136	23/06/81	DE-A-C- 3016106	06/11/80
		GB-A-B- 2051107	14/01/81
		JP-C- 1483991	27/02/89
		JP-A- 55144252	11/11/80
US-A- 4144184	13/03/79	DE-A-B-C 2809045	21/09/78
		GB-A- 1570157	25/06/80
		JP-C- 1178095	30/11/83
		JP-A- 53109633	25/09/78

For more details about this annex : see Official Journal of the European patent Office, No. 12/82