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Tsuchiya et al.

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[54] **PROCESS OF DRY DEVELOPMENT FOR ELECTROPHOTOGRAPHY**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** .... **427/18;** 96/1 SD; 252/62.1

[51] **Int. Cl.** **G03g 13/08;** G03g 9/02

[58] **Field of Search** 252/62.1; 117/17.5

[56] **References Cited**

UNITED STATES PATENTS

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3,236,776	7/1966	Tomanek	252/62.1 P
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[57] **ABSTRACT**

An electrophotographic dry developing process for developing an electric latent image comprises using a dry developer composed of a mixture of toner fine particle and carrier particle, a main particle size of the toner fine particle ranging from 5 to 20 microns, the carrier particle being a mixture of large carrier particles having a main particle size within a range of from 3 times to 10 times the main particle size of the toner fine particle and at least 70% of the large carrier particles being present within a particle size range of from 3 times to 10 times the main particle size of the toner fine particle and smaller carrier particles having a main particle size within a range of the main particle size of toner fine particles ± 5 microns and at least 60% of the small carrier particles being present within a particle size range of the main particle size of toner fine particles ± 5 microns, and the amount of the small carrier particles being 10–85% of the total carrier.

8 Claims, 2 Drawing Figures

FIG. 1

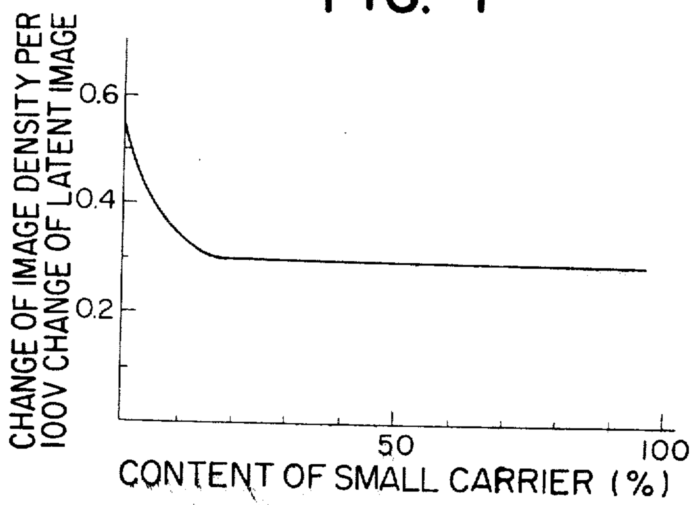
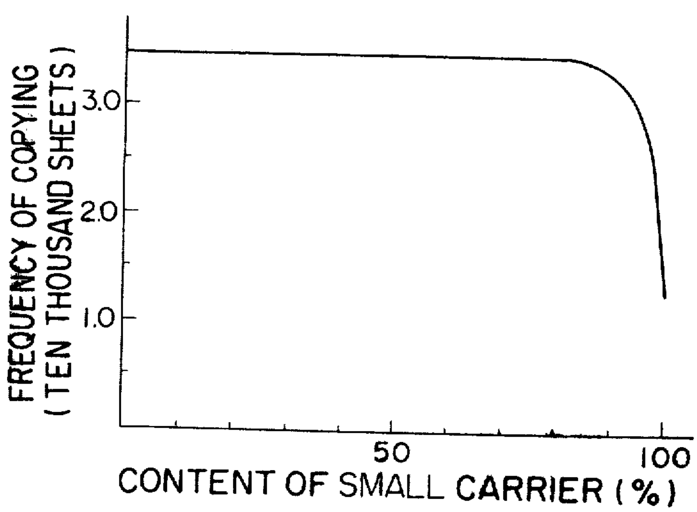

CHANGE OF IMAGE DENSITY PER
100V CHANGE OF LATENT IMAGE
0.6
0.4
0.2
50
100
CONTENT OF SMALL CARRIER (%)

FIG. 2


FREQUENCY OF COPYING
(TEN THOUSAND SHEETS)
3.0
2.0
1.0
50
100
CONTENT OF SMALL CARRIER (%)

PROCESS OF DRY DEVELOPMENT FOR ELECTROPHOTOGRAPHY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a dry developing process for electrostatic image used for electrophotography, electrostatic recording and electrostatic printing.

2. Description of the Prior Art

Heretofore, there have been known various electrophotographic processes such as those disclosed in U.S. Pat. No. 2,297,691, Japanese Pat. No. 23910/1967 and Japanese Pat. No. 24728/1968. In general, there is used a photoconductive material such as zinc oxide, selenium, cadmium sulfide, vinylcarbazole and the like as a photosensitive member, and an electric latent image is formed on the photosensitive member by various means and then the resulting latent image is visualized by using a toner for electrostatic image, and if desired, the image is transferred onto an image receiving sheet such as paper followed by heating to fix the transferred image.

As a conventional developing method, there is a magnet brush developing method. According to this developing method, there is used a dry developer composed of a mixture of a finely devided toner comprising a dye or pigment dispersed in a binder resin and a powder of high magnetic permeability (carrier particle) such as reduced iron powder, iron oxide powder, carbonyl iron powder, ferrite, and sendust alloy powder, and the dry developer is arranged in a brush-like form on a surface of a magnet due to magnetic field of the magnet. By rubbing a surface bearing an electric latent image with this magnet brush, the toner is attracted to the electric latent image to form a visible image.

Originally the feature of the magnet brush developing method resides in that so-called "edge effect" inherent to electrostatic photography is not produced due to the electrode action caused by low electric resistance of carrier iron powder. Usually the magnet brush developer comprises carrier iron powders of about 100–200 microns in particle size and a toner of 5–30 microns in particle size.

The magnet brush developing method is not suitable for reproduction of an original rich in gradation since the resulting visible image since there is hardly produced difference of image density though there is a difference of electrostatic intensity.

It has been found that there is obtained a developer capable of exactly reproducing the difference of electrostatic intensity resulting in excellent reproducibility of gradation when small particle carrier iron powder of about 10 microns in size is used as a magnet brush developer. However, this developer is susceptible to deterioration of performance. The deterioration of performance means phenomena that while the developing procedure is repeated, the reproducibility of high density image is lowered and there is formed fog and further the undesirable edge effect becomes remarkable though the consumed toner is supplemented.

The present inventors have considered that the above mentioned undesirable result is caused by change of the friction charging relation with the toner since the toner is firmly attached to the carrier iron powder. In other words, in case of large particles of carrier iron powder, even when some toner is attached thereto,

such matter is neglected and the performance of developer can be maintained. However, when small particle carrier iron powders are employed, even a very small amount of toner attached to the small particle carrier iron powders causes a remarkable change of performance of the carrier.

A commercial copier usually contains a certain amount of developer in a container and a small portion of toner is periodically added to make up toners consumed during developing procedure while developing operation is repeated several ten thousand times. Therefore, a developer using small particle carriers is not appropriate. Therefore, a toner particle of less than 5 microns in size has been used for improving the reproducibility of gradation in a magnet brush method. This method can relatively improve the reproducibility of gradation, but deterioration of developer still proceeds rapidly though the deterioration velocity is not so fast as that in case of small particle carriers. It is considered that since the toner particle size is small, the toner is packed in hollows on the surface of carrier particles and further a part of toners is fused and consequently the friction chargeability is changed. When such developer is used in a commercial copier, the toner is apt to coagulate and feeding of toner to the developer is not effected uniformly and becomes difficult. Another drawback of the small particle toner is that fog is formed and in case of electrographic process of transferring type, the image is not sufficiently transferred to a web such as paper.

SUMMARY OF THE INVENTION

An object of this invention is to provide a dry developing process for electrophotography capable of solving the above mentioned drawbacks of prior art.

Another object of this invention is to provide a dry developing process of high reproducibility of gradation, free from deterioration of developer and suitable for repeating use.

A further object of this invention is to provide a dry developing method capable of producing a clear and sharp image of high resolving power and free from edge effect and fog.

The present inventors have found that the drawbacks of prior art as mentioned previously can be solved by using large carrier particles and small carrier particles at a certain ratio in a developer containing iron particle carrier for magnet brush developing method. The present invention is based on the above discovery.

According to the present invention, there is provided an electrophotographic dry developing process for developing an electric latent image which comprises using a dry developer composed of a mixture of toner fine particle and carrier particle, a main particle size of the toner fine particle ranging from 5 to 20 microns, the carrier particle being a mixture of large carrier particles having a main particle size within a range of from 3 times to 10 times the main particle size of the toner fine particle and at least 70% of the large carrier particles being present within a particle size range of from 3 times to 10 times the main particle size of the toner fine particle and small carrier particles having a main particle size within a range of the main particle size of toner fine particles ± 5 microns and at least 60% of the small carrier particles being present within a particle size range of the main particle size of toner fine particles ± 5 microns, and the amount of the small carrier particles being 10–85% of the total carrier.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing a relation between content of small carrier and change of image density per 100V change of latent image; and

FIG. 2 is a graph showing a relation between content of small carrier and deterioration of developer and the frequency of copying is counted until the initial image density decreases by 20%.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

By the term "main particle size" is meant a particle size, number of particles having which is the largest in a particle size distribution range. The number of particles is measured by an automatic scanning microscope. A slit is placed on an image surface of optically enlarged particles to be measured and a stage provided with a measuring device automatically scans and a minute change of a transmitting or reflecting light from the sample is converted to an electric signal by a photoelectric multiplier to measure the particle size and the number of particles and determine a particle size of particles, number of which is the largest. This particle size is a main particle size.

As the automatic scanning microscope, there may be used MODEL APM-4 (trade name, manufactured by Union Kogaku K.K.).

As the carrier in the present invention, there may be used conventional carriers for magnet brush developing such as iron oxide powder, reduced iron powder, sendust alloy powder, zinc-magnesium ferrite and carbonyl iron powder.

The developer for the present invention may be produced by the following method. The main particle size of a conventional toner, for example, a toner produced by dispersing carbon black and dye in polystyrene and then pulverising, is measured in a way as mentioned above. Main particle size of conventional developing toner for electrophotographic process usually ranges from 5 to 20 microns, preferred with 8–15 microns. Then, there are prepared large carrier particles which have a main particle size within a range of 3–10 times, preferably 3–6 times, the main particle size of the toner and at least 70%, preferably at least 85%, of the carrier particles is contained in the above mentioned range. Further, there are prepared small carrier particles which have a main particle size within a range of a main particle size of the toner ± 5 microns and at least 60%, preferably at least 80%, of the small carrier particles are contained in the above mentioned range.

These large carrier particles and small carrier particles are mixed in such a manner that the total carrier particles contain the small carrier particles of 10–85% by weight, preferably 30–50% by weight based on the total amount of carrier particles.

One part by weight of the toner may be mixed with 3–30 parts by weight, preferably 5–10 parts by weight, of the carrier mixture as obtained above to produce a dry developer.

The effect of the present invention will be explained by experimental data as shown below.

A toner having the following composition was used.

Polystyrene	100 parts
Carbon black	6 parts
Phthalocyanine Blue (C.I. 74160)	1.5 parts

The above mentioned materials were sufficiently, mixed, fused, cooled, pulverized with a jet mill pulverizer, and classified to obtain toner fine particles having particle size of 8–15 microns and main particle size of 10–11 microns.

One part by weight of the above mentioned toner was mixed with 8 parts by weight of carrier composed of the large carrier particle and the small carrier particle of reduced iron powder having main particle size as shown in the following table at a mixing ratio of 6 to 4 (by weight) to produce a dry developer.

The resulting dry developer was used for developing a latent image by an electrophotographic machine, "Cannon NP-1100" (trade name, supplied by Canon K.K.) of magnet brush type development. The result is shown in the Table below.

Main particle size of large carrier particle	Main particle size of small carrier particle	Image density	Fog density	Gradation reproducibility	Durability	Resolving power
(μ)	(μ)				(thousand sheets)	(lines/mm.)
25–27	12–13	0.68	0.05	0.32	15	11
33–35	12–13	0.90	0.03	0.35	25	10
55–58	12–13	1.15	0.02	0.36	30	10
78–80	12–13	1,32	0.02	0.38	30	10
100–103	12–13	1.45	0.02	0.39	30	9
130–132	12–13	1.60	0.02	0.59	30	6
50–52	4–5	0.70	0.04	0.34	10	10
50–52	7–8	0.90	0.03	0.36	26	10
50–52	10–11	1.00	0.02	0.37	26	10
50–52	13–14	1.10	0.02	0.40	28	9
50–52	16–17	1.12	0.02	0.42	30	8
50–52	25–26	1.21	0.02	0.46	30	7

In the above table, the image density and the fog density were measured by using MACBETH Reflecting Densitometer RD-10. The gradation reproducibility is represented by degree of change of image density per potential change of 100V of electrostatic latent image on a photosensitive member. The durability is represented by number of copies obtained until the initial image density is lowered by 20%.

Change of gradation reproducibility depending upon mixing ratio of large carrier particles and small carrier particles is shown in FIG. 1 and change of durability in FIG. 2.

FIG. 1 is a graph showing the change of image per 100V change of electrostatic latent image wherein the abscissa represents contents of small carrier particles in carrier and the ordinate represents change of image density per 100V change of electrostatic latent image.

FIG. 2 is a graph wherein the abscissa represents the content of small carrier particles and the ordinate represents number of copy obtained in a continuous operation until the initial image density is lowered by 20%.

Form the above table, FIG. 1 and FIG. 2 it is clear that the carrier mixture of the present invention is excellent in image quality, gradation reproducibility, and durability.

The above mentioned result is concerned with data for reduced iron powder, but almost the same result was also obtained when iron oxide powder, sendust alloy powder, carbonyl iron powder and ferrite powder. Different kinds of the iron powder may be mixed.

Adhering of toner fine particle to carrier particle is largely dependent upon particle size ratio of carrier particle to toner fine particle. For example, a dry developer composed of a mixture of large carrier particles and toner fine particles gives undesirable high friction charge so that the fine toner is not easily removed from surface of the carrier particle to cause deterioration of developer. When small particle carrier is mixed with fine toner particle, deterioration is not so easily caused, but there occurs coagulation when relative humidity exceeds 70%. When there is used a developer composed of small particle carrier and toner of relatively large particle size, the carrier particle is adsorbed to the toner particle and thereby the friction chargeability becomes unstable. These various problems can be solved by using the carrier mixture of the present invention.

The following examples will serve to illustrate specific embodiments of the invention.

EXAMPLE 1

Iron oxide powder carrier was produced by mixing large carrier iron oxide powder having a main particle size of 40–42 microns and containing more than 90% of particles ranging from 30 to 60 microns in size being more than 90% of the large carrier particles and small carrier iron oxide powder having a main particle size of 10–11 microns and particles ranging from 8 to 16 microns being about 70% of the small carrier particles at a weight ratio of 7 to 3. The resulting iron oxide powder carrier (800g.) was sufficiently mixed and fused with 100g. of polystyrene, 6g. of carbon black, and 1.5g. of phthalocyanine blue (C.I. 74160), cooled, finely divided by a jet mill.

The resulting iron oxide powder carrier (800g.) was mixed with toner particles having particle size distribution ranging from about 8 to 15 microns and a main particle size of 10–11 microns obtained by sufficiently mixing and fusing with 100g. of polystyrene, 6g. of carbon black, and 1.5g. of phthalocyanine blue (C.I. 74160), cooling, finely deviding by a jet mill, and classifying, and thereby a dry developer was obtained.

The resulting developer was used for developing a latent image by using a commercial dry copier, e.g. "Canon NP 1100" (trade name, supplied by Canon K.K.) of magnet brush developing type. The resulting reproduction gave density change of 0.34 per 100V potential change on a photosensitive plate, excellent gradation reproducibility and clear and sharp images. After development of about thirty thousand times, there is hardly observed change of image quality, and the durability was excellent.

On the contrary, when only large carrier particles were used in the above procedure, the density change was 0.6 per 100V potential change so that high contrast was obtained, but the gradation reproducibility was poor. Further, when only small carrier particles were used in the above procedure, the density change was 0.32 per 100V potential change on the photosensitive plate, but the image density is lowered by about 30%, and after development of about thirty thousand times, there was observed serious deterioration of developing performance and there occurred coagulation.

EXAMPLE 2

The toner (100g.) used in Example 1 was mixed with reduced iron powder (600g.) obtained by mixing large carrier particles composed of reduced iron powders having a main particle size of 50–52 microns and particles ranging from 30 to 80 microns in size being more than 70% and small carrier particles composed of reduced iron powders having a main particle size of 15–16 microns and particles ranging from 5 to 16 microns being 60% at a ratio of 5 to 5 (by weight) and then there was obtained a developer for magnet brush type.

The resulting developer was used for developing in a way similar to Example to produce a clear and sharp copy of high gradation reproducibility. After copying of thirty thousand times, the image density was lowered by less than 15%.

EXAMPLE 3

A toner (100g.) of Example 1 was mixed with sendust alloy powders (600g.) obtained by mixing large carrier particles composed of sendust alloy powders having a main particle size of 70–72 microns and particles ranging from 30 to 100 microns in size being more than 95% of the large carrier particles and small carrier particles composed of sendust alloy powders having a main particle size of 15–16 microns and particles of 10–16 microns in size being 80% of the small carrier particles at a ratio of 4 to 6 (by weight) to produce a developer for magnet brush type. When this developer was used to develop in a way similar to Example 1, a clear and sharp copy of high gradation reproducibility was produced. The change of image density per 100V potential change on the photosensitive member was 0.30. The image density was lowered by 10% after development of thirty thousand times.

EXAMPLE 4

A toner (100g.) of Example 1 was mixed with 700g. of a mixture carrier (700g.) obtained by mixing large carrier particles composed of zinc-magnesium ferrite powder having a main particle size of 90–92 microns and particles ranging from 30 to 100 microns in size being more than 90% of the large carrier particles and small carrier particles composed of reduced iron powders having a main particle size of 12–13 microns and particles ranging from 5 to 16 microns in size being more than 90% of the small carrier particles at a ratio of 6 to 4 (by weight) to produce a developer for magnet brush type. The resulting developer was used for developing in a way similar to Example 1 to produce a clear and sharp copy of high gradation reproducibility. The change of image density per 100V potential change on the photosensitive member was 0.39. After development of thirty thousand times, the image density was lowered by less than 10%.

EXAMPLE 5

A toner (100g.) similar to that of Example 1 except that the main particle size was 15–16 microns and the particle size distribution ranges from about 8 to 25 microns, was mixed with a mixture carrier (800g.) obtained by mixing large carrier particles composed of carbonyl iron powders having a main particle size of 100–102 microns and particles ranging from 50 to 150 microns in size being more than 90% of the large carrier particles and small carrier particles composed of reduced iron powders having a main particle size of 18–19 microns and the particles ranging from 13 to 25 microns in size being more than 90% of the small carrier particles at a ratio of 4 to 6 (by weight) to produce a developer for magnet brush type.

Development was conducted by using the resulting developer in a way similar to Example 1 to produce a clear and sharp copy of high gradation reproducibility. The change of image density per 100V potential change was 0.38. After development of thirty thousand times, the image density was lowered by about 15%.

EXAMPLE 6

A toner (100g.) similar to that of Example 1 except that a main particle size was 7–8 microns and the particle size distribution ranging from 3 to 18 microns was mixed with iron oxide powders (600g.) obtained by mixing large carrier particles composed of iron oxide powders having a main particle size of 58–60 microns and the particles ranging from 25 to 80 microns in size being more than 80% of the large carrier particles and small carrier particles composed of iron oxide powders having a main particle size of 10–11 microns and the particles ranging from 5 to 13 microns being more than 70% of the small carrier particles at a ratio of 8 to 2 (by weight) to produce a developer for magnet brush type.

The resulting developer was used for developing in a way similar to Example 1 to produce a clear and sharp copy of high gradation reproducibility. The change of image density per 100V potential change on the photosensitive member was 0.30, and the image density was lowered by about 20% after development of thirty thousand times.

EXAMPLE 7

A toner (100g.) having a main particle size of 10–11 microns and particle size distribution ranging from 8 to 15 microns produced by fusing 100g. of epoxy resin, 5g. of nigrosive and 8g. of carbon black, cooling, finely dividing by a jet mill pulverizer and classifying, was mixed with a mixture carrier (800g.) comprising large carrier particles composed of carbonyl iron powders having a main particle size of 60–62 microns and the particles ranging from 40 to 80 microns in size being more than 80% of the large carrier particles and small carrier particles composed of reduced iron powders having a main particle size of 10–11 microns and the particles ranging from 5 to 16 microns in size being more than 90% at a ratio of 6 to 4 (by weight) to produce a developer for magnet brush type. The resulting developer was used for developing an electrostatic latent image on a zinc oxide paper by a commercially available copier, e.g. "Canofax 1000" (trade name, manufactured by Canon K.K.) to produce a clear and sharp copy of high gradation reproducibility. The change of image density per 100V potential change on a photosensitive paper was 0.35. The image density was lowered by less than 15% after development of thirty thousand times.

On the contrary, when only the large carrier particle composed of carbonyl iron powder was used in the above procedure, the image density was high, but the gradation reproducibility was poor, and change of image density per 100V potential change was 0.48.

When only the small carrier particle was used in the above procedure, the gradation reproducibility was good, but the developer was deteriorated after about 500 sheets of copy was reproduced and the image density was lowered by about 30%.

We claim:

1. An electrophotographic magnetic brush developing process for developing an electric latent image which comprises using a dry developer composed of a mixture of finely divided colored resinous toner particles and magnetic carrier particles, the ratio of toner to carrier being 1:3 to 1:30, a main particle size of the finely divided colored resinous toner particles ranging from 5 to 20 microns, the magnetic carrier particles being a mixture of magnetic large carrier particles having a main particle size within a range of from 3 times to 10 times the main particle size of the toner particles and at least 70% of the large carrier particles being present within a particle size range of from 3 times to 10 times the main particle size of the toner particles and magnetic small carrier particles having a main particle size within a range of the main particle size of toner particles ± 5 microns and at least 60% of the small carrier particles being present within a particle size range of the main particle size of toner particles ± 5 microns, and the amount of the small carrier particles being 10–85% of the total carrier.

2. An electrophotographic magnetic brush developing process according to claim **1** in which the main particle size of the toner particles is 8–15 microns.

3. An electrophotographic magnetic brush developing process according to claim **1** in which the large carrier particles have a main particle size within a range of from 3 times to 6 times the main particle size of the toner particles and at least 85% of the large carrier particles is present within a particle size range of from 3 to 6 times the main particle size of the toner particles.

4. An electrophotographic magnetic brush developing process according to claim **1** in which the amount of small carrier particles is 30–50% of total amount of the total carrier.

5. An electrophotographic magnetic brush developing process for developing an electric latent image which comprises using a dry developer composed of a mixture of finely divided colored resinous toner particles and magnetic carrier particles, the ratio of toner to carrier being 1:5 to 1:10, a main particle size of the finely divided colored resinous toner particles ranging from 5 to 20 microns, the magnetic carrier particles being a mixture of magnetic large carrier particles having a main particle size within a range of from 3 times to 6 times the main particle size of the toner particles and at least 85% of the large carrier particles being present within a particle size range of from 3 times to 6 times the main particle size of the toner particles and magnetic small carrier particles having a main particle size within a range of the main particle size of toner particles ± microns and at least 80% of the small carrier particles being present within a particle size range of the main particle size of toner particles ± 5 microns, and the amount of the small carrier particles being 30–50% of the total carrier.

6. An electrophotographic magnetic brush developing process according to claim **1** wherein the toner particles comprise colored polystyrene.

7. An electrophotographic magnetic brush developing process according to claim **1** wherein the toner particles comprise colored epoxy resin.

8. An electrophotographic magnetic brush developing process according to claim **1** wherein the carrier particles comprise at least one member selected from the group consisting of iron oxide, reduced iron, sendust alloy, zinc magnesium ferrite, and iron carbonyl compound.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,895,125 Dated July 15, 1975

Inventor(s) KAICHI TSUCHIYA, ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, line 12, "smaller" should read --small--;

Column 1, line 14, "24728" should read --24748--;

Column 1, line 27, "devided" should read --divided--;

Column 3, line 24, "electric" should read --electronic--;

Column 4, line 40, "Cannon" should read --Canon--;

Column 5, line 62, "cooling, finely deviding" should read --cooled, finely divided--;

Column 5, lines 62 and 63, "classifying" should read --classified--.

Signed and Sealed this

seventh **Day of** *October 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks