⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number : **0 618 509 A1**

## ⑫ EUROPEAN PATENT APPLICATION

㉑ Application number : **94400679.0**

(51) Int. Cl.$^5$ : **G03G 7/00**

㉒ Date of filing : **30.03.94**

㉚ Priority : **31.03.93 US 40876**

㊸ Date of publication of application :
**05.10.94 Bulletin 94/40**

(84) Designated Contracting States :
**AT DE FR GB IT**

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# (54) Electrophotographic toner receptive release coatings.

(57) A release coating receptive to toner particles emitted by electrophotoconductive devices comprises a polymer having at least one vinyl polymeric segment having a $T_g°$ between -10°C and 65°C and at least one siloxane polymeric segment.

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## Field of the Invention

The present invention relates to release coatings. In particular, the present invention relates to release coatings which anchor toner.

## Background of the Invention

A number of conventional electrophotoconductive devices such as printers and copiers employ dry toner. These printers and/or copiers employ toner to form a latent image transferable from an imaging device to a substrate such as paper, tag or label stock. The toned latent image is then subjected to heat fusing in order to obtain the best print quality and toned image density.

Although the resulting images are often of good quality, there are problems associated with the imaging processes employed by printers and/or copiers. For example, there is the problem of backgrounding which is the accumulation of various unwanted materials such as toner particles on the substrate. Backgrounding can occur when the imaging device evenly disperses toner particles over a non-imaged area of the substrate.

Additional backgrounding problems can be experienced when label stock is utilized. Label stock comprises one or more non-continuous substrates referred to as labels which are adhered by an adhesive to a protective backing or liner. To permit the label to be removed from the protective liner, it is customary to coat a release coating over the liner in order to permit ready separation of the two members.

Although the release coating permits ready separation, detrimental backgrounding problems can be experienced when a partially used sheet of label stock is repassed through an electrophotoconductive printing device. Usually after the first printing, one or more labels are removed thereby exposing the release coating. Thus, backgrounding occurs not only on the label, but also upon exposed release coating. The toner will not anchor to conventional silicone release coatings due to the fact that these coatings have a different polarity than do the toner particles and because the silicone coatings have much lower glass transition temperatures than the toner particles. Therefore, the unwanted particles which are dispersed on the release coating tend to flake off the coating, then transfer to rollers found in printers and then possibly, relocate themselves to the succeeding labels or sheets.

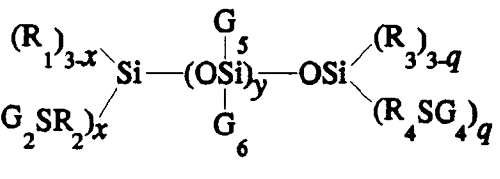
World Patent Application No. US/90/03286 (Josephy et al.) describes a toner receptive coating which can be applied to compressible substrates such as paper. Similarly, U.S. Patent No. 4,492,410 (Fitch et al.) describes a toner receptive coating applied to substrates such as paper. However, neither of these two references teach the use of a release coating which can also anchor toner particles.

Thus, there currently exists a need for a release coating which will anchor toner particles and yet, maintains good release properties for substrates such as labels.

## Summary of the Invention

The present invention comprises a release coating which is capable of anchoring toner particles emitted by electrophotoconductive devices and yet, maintains good release properties. The release coating of the present invention is coated onto a liner over which one or more substrates such as labels can be applied. The coating comprises a polymer having at least one vinyl polymeric segment having a Tg between -10°C and 65°C and at least one siloxane polymeric segment. Preferably, the $T_g$ should be between 20°C and 45°C of the vinyl polymer segment.

In one embodiment of the present invention, the coating is a copolymer which comprises the formula:



$$\begin{matrix}(R_1)_{3-x} \\ (G_2SR_2)_x\end{matrix}\!\!>\!Si-(O\overset{G_5}{\underset{G_6}{Si}})_y-OSi\!<\!\!\begin{matrix}(R_3)_{3-q} \\ (R_4SG_4)_q\end{matrix}$$

wherein

$R_1$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_2$ can independently be the same or different and are divalent linking groups;

$R_3$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_4$ can independently be the same or different and are divalent linking groups;
x is an integer of 0 to 3;
y is an integer of 10 or greater;
q is an integer of 0 to 3;

$G_5$ and $G_6$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoralkyl, hydrogen, and -WSA wherein W is a divalent linking group and A is defined below; and

$G_2$ and $G_4$ are A wherein A is a vinyl polymeric segment or block consisting essentially of a polymerized free radically polymerized monomer.

In another embodiment of the present invention, the coating comprises a copolymer of D and E monomers copolymerized to form a polymeric backbone with F monomer grafted thereto wherein:

D is at least one free radically polymerizable vinyl monomer;
E is at least one polar monomer copolymerizable with D, the amount of E being up to 30% of the total weight of all monomers, and
F is a monomer having the general formula $X\text{-}(Y)_nSiR_{(3-m)}Z_m$ wherein
  X is a vinyl group copolymerizable with the D and E monomers,
  Y is a divalent linking group where n is zero or 1;
  m is an integer of 1 to 3;
  R is hydrogen, lower alkyl (e.g., methyl, ethyl, or propyl), aryl (e.g., phenyl or substituted phenyl), or alkoxy groups; and
  Z is a monovalent siloxane polymeric moiety having a number average molecular weight above about 1,000 and is essentially unreactive under copolymerization conditions.

The present invention also includes a toner receptive article comprising a liner, a release coating and a substrate such as a label mounted over the liner.

## Drawings

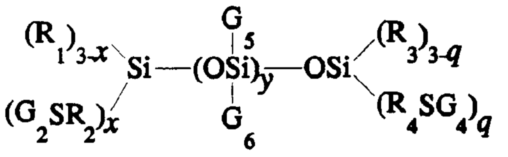
Fig. 1 is a representation of an embodiment of Applicants' invention tested in accordance with the procedures described below.

Fig. 2 is a representation of Avery 30-up stock #5160 which has been tested in accordance with the procedures described below.

## Detailed Description

The present invention includes a release coating which is capable of anchoring toner. The release coating has at least one siloxane polymeric segment and at least one vinyl polymeric segment having a $T_g$ between -10°C and 65°C. By virtue of its chemical composition and structure and the resultant properties, the release coating is well-suited to control toner anchorage applications. In particular, it is thought that the silicone segment presents a low energy, "siliconized" release surface and the higher energy vinyl polymeric segment provides the adhesion for the toner particles.

In one embodiment of the present invention, the coating is a copolymer which comprises the formula:

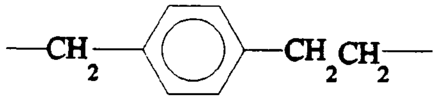


$$(R_1)_{3-x}(G_2SR_2)_x\text{Si}-(\text{OSi}(G_5)(G_6))_y-\text{OSi}(R_3)_{3-q}(R_4SG_4)_q$$

$R_1$ are monovalent moieties which can independently be the same or different which are selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, hydroxyl, fluoroalkyl, and hydrogen. Preferably, $R_1$ are monovalent moieties which can independently be the same or different selected from the group consisting of $C_{1-4}$ alkyl and hydroxyl. Most preferably, $R_1$ is selected from the group consisting of methyl and butyl.

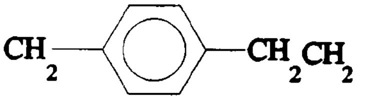
$R_2$ are divalent linking groups which can independently be the same or different. Suitable divalent linking groups include but are not limited to the following: $C_1$ to $C_{10}$ alkylene, arylene, alkylarylene and alkoxyalkylene. Preferably, $R_2$ is selected from the group consisting of $C_{1-3}$ alkylene and $C_7$-$C_{10}$ alkylarylene due to ease of synthesis of the compound. Most preferably, $R_2$ is selected from the group consisting of $-CH_2-$ ; 1,3-propylene;

and



$R_3$ are monovalent moieties which can independently be the same or different which are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl and fluoroalkyl, and hydrogen. Preferably, $R_3$ are monovalent moieties which can independently be the same or different selected from the group consisting of $C_{1-4}$ alkyl and hydroxyl. Most preferably, $R_3$ is selected from the group consisting of methyl and butyl.

$R_4$ are divalent linking groups which can independently be the same or different. Suitable divalent linking groups include but are not limited to the following: $C_1$ to $C_{10}$ alkylene, arylene, alkylarylene and alkoxyalkylene. Preferably, $R_4$ is selected from the group consisting of $C_{1-3}$ alkylene and $C_7$-$C_{10}$ alkylarylene for reasons of ease of synthesis. Most preferably, $R_4$ is selected from the group consisting of $-CH_2-$; 1,3-propylene; and



$G_5$ and $G_6$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, fluoralkyl, hydrogen, and -WSA wherein W is a divalent linking group and A is defined below.

W are divalent linking groups. Suitable divalent linking groups include, but are not limited to, $C_1$ to $C_{10}$ alkylene, alkarylene, arylene, and alkoxyalkylene. Preferably, W is selected from the group consisting of methylene and propylene.

$G_2$ and $G_4$ are the same or different and comprise A. A is a vinyl polymeric segment consisting essentially of polymerized free radically polymerizable monomer. A can comprise either a homopolymer segment or block or a copolymer segment or block. The toner anchorage properties of the coating are determined by the vinyl polymeric segment content. The chemical nature or composition of the vinyl polymeric segments can be modified independent of the release aspect to improve toner anchorage and adhesion to the substrate. Thus, the release coating can be chemically tailored to provide a specific level of toner anchorage. The selection of the composition of A is typically based upon the intended use of the release coating and the properties the release coating must possess in order to accomplish its intended purpose.

A can include, but is not limited to, those monomers wherein the free radically polymerizable monomer or monomers are chosen such that a vinyl segment has a $T_g$ or $T_m$ above about -20°C. The preferred free radically polymerizable monomers are selected from the group consisting of styrene, methyl methacrylate, methyl acrylate, acrylic acid, methacrylic acid, acrylonitrile, isobornyl acrylate, isobornyl methacrylate, N-vinyl pyrrolidone, butyl methacrylate, isopropyl methacrylate, vinyl acetate, hydroxy propylacrylate, hydroxy ethyl acrylate and mixtures thereof.

The amount and composition of the vinylic segment to silicone should range from about 98 to about 2 parts preferably, from about 40 to about 60 parts by weight. It is preferred that the vinyl polymeric segments should have a molecular weight in the range of 2,000 to 80,000, more preferably 5,000 to 50,000.

The release properties of the coating are determined by both the silicone content (weight percentage) present in the copolymer and the molecular weight of the silicone segment, with higher silicone content and/or molecular weight providing easier release. A copolymer or copolymer blend can, therefore, be chemically tailored to provide a specific level of release which can be reproduced with consistency, thus making possible the variation of the release properties of a liner over a range of values in a controlled fashion.

The silicone polymeric segment must have an average molecular weight above about 1000 in order for the release coating to function properly. Preferably, the silicone polymeric segment has a number average molecular weight of about 1000 to about 20,000. Most preferably, the silicone polymeric segment has a number average molecular weight ranging from about 2,000 to about 15,000. The silicone polymeric segment can comprise about 2 to 60 wt% of the release coating in order to allow for a wide range of release performance.

In another embodiment of the present invention, the release coating comprises a copolymer of D and E monomers copolymerized to form a polymeric backbone. Grafted to the backbone is an F monomer. The D and E monomers provide the toner anchorage properties of the coating and the F monomer provides the release properties.

The D monomer or monomers (there may be more than one) are chosen such that the backbone $T_g$ or $T_m$ is above about -20°C. Representative examples of D monomers include styrene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile and acrylic or methacrylic acid esters of nontertiary alcohols or tertiary alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, cyclohexanol, benzyl alcohol, dodecanol, hexadecanol, and octadecanol, the alcohols having from 1 to 18 carbon atoms.

Especially preferred D monomers include methyl methacrylate, butyl methacrylate, vinyl acetate, partially hydrolyzed vinyl acetate, methyl acrylate and octadecyl acrylate.

Representative E monomers useful in practicing the invention, and which may be used either individually or in combination, include carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and 2-carboxyethyl acrylate and their ammonium or metal salts; sulfonic or phosphonic acids such as 2-sulfoethyl methacrylate, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, styrene sulfonic acid, and vinyl benzyl phosphonic acid and their ammonium or metal salts; amides such as acrylamide, methacrylamide, N,N-dimethyl acrylamide, and N-vinyl pyrrolidone; and monomers having hydroxyl functionality (e.g., 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, and dihydroxypropyl acrylate), ammonium functionality derived from reaction of amine-containing monomers (e.g., N,N,-dimethylaminoethyl methacrylate and vinyl pyridine) with alkylating agents or protic acids, or zwitterionic functionality such as that derived by reaction of amine monomers with hydrogen peroxide or propane sulfone.

The F monomer has the general formula:

$$X\text{-}(Y)_nSiR_{(3-m)}Z_m$$

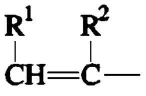
X is a vinyl group copolymerizable with the D and E monomers.

Y is a divalent linking group.

R comprises hydrogen, lower alkyl groups such as methyl, ethyl, or propyl, aryl groups such as phenyl or substituted phenyl and alkoxy groups such as methoxy and ethoxy groups.

Z is a monovalent siloxane polymeric moiety having a number average molecular weight above about 1,000 and is essentially unreactive under copolymerization conditions.

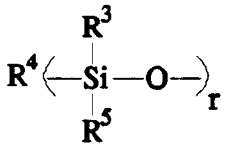
The preferred F monomer may be further defined as having an X group which has the general formula



$$\overset{R^1}{\overset{|}{CH}}=\overset{R^2}{\overset{|}{C}}-$$

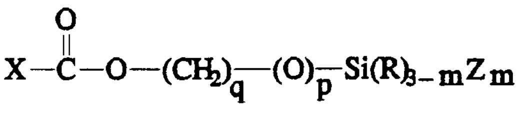
wherein $R^1$ is a hydrogen atom or a COOH group and $R^2$ is a hydrogen atom, a methyl group, or a $CH_2COOH$ group.

The Z group of the F monomer has the general formula



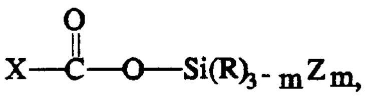
$$R^4\Big(-\underset{\underset{R^5}{|}}{\overset{\overset{R^3}{|}}{Si}}-O-\Big)_r$$

wherein $R^3$ and $R^5$ are independently lower alkyl, aryl, or fluoroalkyl, where lower alkyl and fluoroalkyl both refer to alkyl groups having from one to three carbon atoms and where aryl refers to phenyl or substituted phenyl. $R^4$ may be alkyl, alkoxy, alkylamino, aryl, hydroxyl, or fluoroalkyl, and r is an integer from about 5 to about 700. Preferably, the F monomer has a general formula selected from the group consisting of the following, where m is 1, 2 or 3, p is zero or 1, R" may be alkyl or hydrogen, and X, R, and Z are as defined above:

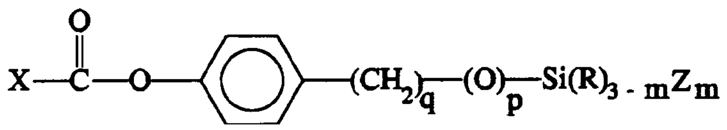


$$X-\overset{\overset{O}{\|}}{C}-O-(CH_2)_q-(O)_p-Si(R)_{3-m}Z_m$$

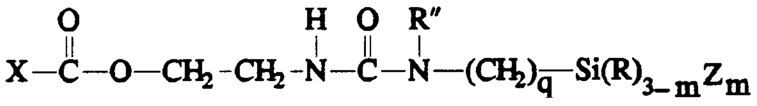
wherein q is an integer from 2 to 6;



$$X-\overset{O}{\overset{\|}{C}}-O-Si(R)_{3-m}Z_m,$$

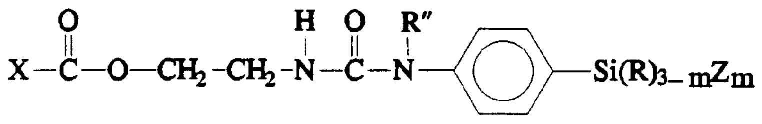


wherein q is an integer from zero to 2;

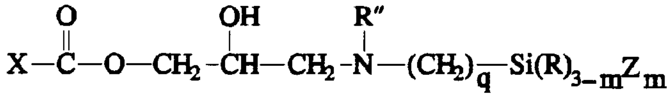


$$X-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{R''}{\overset{|}{N}}-(CH_2)_q-Si(R)_{3-m}Z_m$$

wherein q is an integer from 2 to 6;



and



$$X-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{R''}{\overset{|}{N}}-(CH_2)_q-Si(R)_{3-m}Z_m$$

wherein q is an integer from 2 to 6.

The release coating of the present invention may comprise the copolymers of the two embodiments alone, or may comprise copolymers blended with other compatible homopolymers and/or copolymers. The low percentage of silicone contained in the copolymers makes the copolymers readily compatible with polymers of similar composition to the vinyl Polymeric blocks or segments. In addition, there are several pairs of dissimilar polymers that yield compatible blends due to specific interaction as described by S. Krause in Polymer Blends, Academic Press, New York, 1978. Introduction of a low level of silicone block onto one of these polymers will not influence compatibility.

In addition, additives, fillers or pigments such as alumina, silica, titanate, or calcium carbonate may, of course, be added to the copolymer compositions.

The release coating of the present invention should provide sufficient anchorage to anchor at least 50% of the toner. It is understood that "substantially" means at levels of at least 50%. More preferably, it should anchor at least 70% of the toner.

In addition, the release coating should have a surface release value not greater than about 10 oz./in (11 N/dm). It should be understood that this upper limit applies to use with highly aggressive pressure-sensitive adhesives (PSAs) which have peel adhesion values of 45 N/dm or higher. PSAs as a group fall into three broad categories (1) low (5-15 N/dm), (2) intermediate (25-50 N/dm), and (3) high (60-100 plus N/dm) peel adhesion ranges. It is apparent that the degree of release can be selected to match the aggressiveness of the PSA with which it will be in contact and it is only for the most aggressive PSAs that a release value as high as 10 oz/in. (11 N/dm) would be selected. Release coatings for less aggressive PSAs would be selected to be correspondingly lower.

The release compositions do not require curing or crosslinking; however, if solvent resistance is desired for a particular application, crosslinking can be effected by standard methods well-known in the art, such as radiation curing (electron beam or ultraviolet light) or chemical crosslinking.

The release coating compositions may be applied to any suitable backing or liner by means of conventional coating techniques such as wire-wound rod, direct gravure, offset gravure, reverse roll, air-knife and trailing blade coating. Suitable liners include paper, non-woven fabrics and films of thermoplastic resins such as polyesters, polyamides, polyolefins, polycarbonates and polyvinyl chloride.

In addition, any substrate which can be applied to a liner by a pressure sensitive adhesive can be utilized. For example, paper is a suitable substrate.

In a preferred embodiment, the release coating of the present invention is utilized as a component of label stock. In this preferred embodiment, one or more non-continuous substrates such as labels are adhered to protective liner by a suitable adhesive. To permit the substrate to be removed from the liner, the release coating of the present invention is coated the liner.

The following examples are illustrative in nature and are not intended to limit the invention in any way.

## TEST SAMPLES

The polymer solutions of Examples 1 to 19 discussed below were diluted to 15% solids in distilled water. The solutions were then coated onto commercially available roll base paper with a gravure roll having a pyramidal pattern of 200 cells per inch. A two roll direct gravure coating was applied to each sample. Two different roll base papers were utilized. Supercalendered C1S paper supplied by the Simpson Paper Company was coated with the diluted polymer solutions of Examples 1 to 4 and machine glazed base paper sold by Akrosil were coated with the diluted polymer solutions of Examples 4 to 19. After coating, the base papers were dried at 77°C.

## Test Methods

### Release Properties

The release property of an adhesive refers to ease that an adhesive separates from another surface. It is the force required to remove a flexible adhesive tape from a test sample at a specific angle and rate of removal. It is measured in Newtons per decimeter (N/dm) Two test methods are used to evaluate the release properties of coated flexible sheet materials. Both tests are modified versions of the industry standard peel adhesion test ASTM D3330-78 PSTC 1 and 3 used to evaluate PSA coated materials. The two modified release property tests are described below.

### 1. Immediate Release Value

Each test sample was conditioned overnight at constant temperature (22°C) and humidity (50% RH). Thereafter, a 5.08 cm by 25.4 cm strip of the test sample is laminated to a constant 90° angle jig commercially available as the Deltron Ball Slide from the J.R. Brass Co. of Eden Praire, MN with double coated tape. Then a 2.54 cm strip of a PSA coated test tape was rolled down onto the laminate with a 1.82 kg rubber roller. The force required to remove this tape at 90° and 30.5 cm/minute was then measured was measured by a Sintech/Instron Tensile Tester System commercially available from Sintech Corporation, a division of MTS Systems Corporation, Research Triangle Park, North Carolina.

### 2. Aged Release Test

The aged release test was conducted in the same manner as the immediate release test with the exception that the test tape was allowed to dwell in contact with the coated paper for 3 days at 65°C and 50% RH, 11 days at 21°C and 80% RH, 11 days at 49°C dry, and 11 days 49°C at 65% RH, prior to removal.

### Toner Receptivity Testing

The toner receptivity of the test samples was assessed by printing on a 21.6 cm x 27.9 cm test sample an asterisk pattern, i.e., (****), in an Hewlett Packard LaserJet II printer. The imaged coated sheets then sat overnight in a controlled environment of 21°C and 50% RH. Thereafter, a 2.54 cm x 25.4 cm strip of Scotch™ Brand 810™ tape manufactured by the Minnesota Mining and Manufacturing Company was rolled down over the imaged test samples using two passes of a 1.82 kg rubber roller. After the two passes, the test samples were allowed to sit in a controlled environment of 21°C and 50% RH for 24 hours. Then the Scotch™ Brand 810™ tape was laminated image side up to the stage of in TIMI Release and Adhesion Tester sold by Testing Machines Inc. of Mityville, New York with double coated tape. The 810™ tape was then removed at a peel angle of 180°C at 3048 cm/minute. Image analysis was used to determine the amount of toner which remained anchored to the coated sheet.

## Abbreviations

AA - acrylic acid
AIBN - 2-2'-azobisbutyronitrile
BMA - butyl methacrylate
EMA - ethyl methacrylate
IPA - isopropyl alcohol
KF2001 - a mercaptofunctional dimethyl siloxane with 4-5 mole % mercapto functionality commercially available from Shin-Etsu.
MA - methacrylic acid
MAA - methyl acrylate
MEK - methyl ethyl ketone
MMA - methyl methacrylate
ODA - octadecyl acrylate

## Example 1

The composition of Example 1 was prepared in the following manner:

First, a solvent borne sample was prepared by charging a 32 oz. reaction bottle with 45 grams of mercaptofunctional dimethyl siloxane with 4-5 mole % mercapto functionality commercially available as KF-2001 from Shin-Etsu, 169 grams of methyl acrylate, 11 grams acrylic acid, 335 grams of methyl ethyl ketone (MEK) and 0.56 grams 2-2'-azobisisobutyronitrile (AIBN). The solution mixture was then purged with nitrogen for 2 minutes at a rate of 1 L/min, after which the bottle was sealed. The sealed bottle containing the clear solution was tumbled in a constant temperature bath for 20 hours at 55°C resulting in a viscous cloudy white solution.

Thereafter, a waterborne solution was prepared by filling a gallon jar with 860 grams deionized (DI) water and 9 grams $NH_4OH$. Next, 537 grams of the solvent borne solution (40.0 % solids) was added to the solution in the gallon jar. The resulting solution was placed on a shaker and shaken for one-half hour in order to complete the neutralization. The MEK was then stripped from the resulting viscous solution on a rotary evaporator at 40°C using an aspirator vacuum to yield 19.0 % solids aqueous solution. An additional amount of DI water was added to obtain 15.0 % solids solution. The ingredients utilized in forming a solvent borne solution and water borne solution and the amount of the ingredients utilized are reported in Tables 1 and 2 respectively. The ingredients of the release coating, the weight percentage of the ingredients and the test results are reported in Table 3.

## Examples 2-20

The copolymers of Examples 2-20 were prepared in accordance with the procedure outlined in Example 1. The ingredients utilized in forming a solvent borne solution and water borne solution and the amount of the ingredients utilized are reported in Tables 1 and 2 respectively. The ingredients of the release coating, the weight percentage of the ingredients and the test results are reported in Table 3.

TABLE 1

| Example | Ingredients Utilized in Polymerization | Amount of Ingredients Utilized (gms.) |
|---|---|---|
| 1 | KF2001/MA/AA/MEK/AIBN | 45/169/11/335/0.56 |
| 2 | KF2001/MA/AA/MEK/AIBN | 25/70/10/157.5/0.52 |
| 3 | KF2001/MA/AA/MEK/AIBN | 50/140/20/315/0.53 |
| 4 | KF2001/MA/MAA/MEK/AIBN | 50/140/10/300/0.5 |
| 5 | KF2001/MA/MAA/MEK/AIBN | 52/182/26/390/0.65 |
| 6 | KF2001/MA/MAA/MEK/AIBN | 62/173/25/390/0.65 |
| 7 | KF2001/MA/MAA/MEK/AIBN | 60/140/20/330/0.55 |
| 8 | KF2001/MA/MAA/MEK/AIBN | 60/140/10/315/0.53 |
| 9 | KF2001/MA/MAA/MEK/AIBN | 50/120/10/300/0.5 |
| 10 | KF2001/MA/MAA/MMA/MEK/AIBN | 65/130/13/52/390/0.65 |
| 11 | KF2001/MA/MAA/MMA/MEK/AIBN | 30/75/7.5/37.5/225/0.38 |
| 12 | KF2001/MA/MAA/MMA/MEK/AIBN | 37.5/60/7.5/45/225/0.38 |
| 13 | KF2001/MA/MAA/MMA/MEK/AIBN | 37.5/45/7.5/60/225/0.38 |
| 14 | KF2001/MA/MAA/MMA/MEK/AIBN | 37.5/30/7.5/75/225/0.38 |
| 15 | KF2001/MA/MAA/MMA/MEK/AIBN | 39.5/71/7.9/31.6/225/0.38 |
| 16 | KF2001/MA/MAA/MMA/MEK/AIBN | 35.7/78.6/7.1/28.6/225/0.38 |
| 17 | KF2001/MA/MAA/MMA/MEK/AIBN | 34.1/81.8/6.8/27.3/225/0.38 |
| 18 | KF2001/MA/MAA/MMA/MEK/AIBN | 32.6/84.8/6.5/26.1/225/0.38 |
| 19 | KF2001/MA/MAA/MMA/MEK/AIBN | 31.2/87.5/6.2/25/225/0.38 |
| 20 | KF2001/MA/MAA/MMA/MEK/AIBN | 50/100/10/40/300/1.0 |

TABLE 2

| Example | Ingredients Utilized In Preparation of Water-borne Solution | Amount of Ingredients Utilized (gms.) |
|---|---|---|
| 1 | Polymer[1]/$NH_4OH/H_2O$ | 537/9/860 |
| 2 | Polymer/$NH_4OH/H_2O$ | 537/9.0/645 |
| 3 | Polymer/$NH_4OH/H_2O$ | 520/8.8/650 |
| 4 | Polymer/$NH_4OH/H_2O$ | 326/5/540 |
| 5 | Polymer/$NH_4OH/H_2O$ | 320/9/500 |
| 6 | Polymer/$NH_4OH/H_2O$ | 320/8/500 |
| 7 | Polymer/$NH_4OH/H_2O$ | 321/540/9 |
| 8 | Polymer/$NH_4OH/H_2O$ | 325/5/540 |
| 9 | Polymer/$NH_4OH/H_2O$ | 317/5/540 |
| 10 | Polymer/$NH_4OH/H_2O$ | 320/4.3/500 |
| 11 | Polymer/$NH_4OH/H_2O$ | 360/7.5/576 |
| 12 | Polymer/$NH_4OH/H_2O$ | 345/4.6/530 |
| 13 | Polymer/$NH_4OH/H_2O$ | 345/4.7/530 |
| 14 | Polymer/$NH_4OH/H_2O$ | 345/4.6/520 |
| 15 | Polymer/$NH_4OH/H_2O$ | 340/5/530 |
| 16 | Polymer/$NH_4OH/H_2O$ | 340/4.4./530 |
| 17 | Polymer/$NH_4OH/H_2O$ | 340/4.2/530 |
| 18 | Polymer/$NH_4OH/H_2O$ | 340/4/530 |
| 19 | Polymer/$NH_4OH/H_2O$ | 340/4/530 |
| 20 | Polymer/$NH_4OH/H_2O$ | 480/5/760 |

---

[1] The polymer is the reaction product of KF2001, MA and AA and/or MAA or MMA.

Table 3

| Ex. | Ingredients | wt % Ingred-ients | Tg° C | Tape | Release g/inch | | | | | | Percentage Toner receptivity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Initial | 3 days 150°F dry | 11 days | | | | |
| | | | | | | | 70°F, 50% RH | 70°F, 80% RH | 120° dry | 120°F, 65% RH | |
| 1 | MA/KF2001/AA | 75/20/5 | 11 | A | 51 | 211 | 69 | 63 | 73 | 146 | 8 |
| 2 | MA/KF2001/AA | 70/25/10 | 16 | A | 10 | 181 | 29 | 63 | 51 | 221 | 75 |
| 3 | MA/KF2001/AA | 70/25/5 | 20 | A | 15 | 145 | 50 | 91 | 45 | 67 | 68 |
| 4 | MA/KF2001/MAA | 70/25/5 | 18 | A | 8 | 142 | 27 | 50 | 49 | 104 | 88 |
| 5 | MA/KF2001/MAA | 70/20/10 | 26 | A | 10 | 29 | 20 | 68 | 35 | 63 | 56 |
| 6 | MA/KF2001/MAA | 70/25/10 | 26 | A | 9 | 31 | 56 | 75 | 41 | 59 | 38 |
| 7 | MA/KF2001/MAA | 70/30/10 | 26 | A | - | 31 | 11 | 30 | 34 | 36 | 25 |
| 8 | MA/KF2001/MAA | 70/30/5 | ? | A | - | 73 | 14 | 44 | 87 | 138 | 22 |
| 9 | MA/KF2001/MMA/MAA | 60/25/10/5 | ? | A | - | 60 | 16 | 33 | 67 | 85 | 58 |
| 10 | MA/KF2001/MMA/MAA | 50/25/20/5 | 40 | A | 14 | 51 | 46 | 46 | 74 | 46 | 92 |
| 11 | MA/KF2001/MMA/MAA | 50/20/25/5 | 44 | A | 23 | 53 | 71 | 65 | 73 | 87 | 78 |
| 12 | MA/KF2001/MMA/MAA | 40/25/30/5 | 18 | A | 34 | 57 | 189 | 68 | 57 | 58 | 75 |
| 13 | MA/KF2001/MMA/MAA | 30/25/40/5 | 22 | A | 88 | 64 | 310 | 305 | 120 | 83 | 64 |

| Ex. | Ingredients | wt % Ingredients | Tg° C | Tape | Release g/inch |  |  |  |  |  |  | Percentage Toner receptivity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Initial | 3 days 150°F dry | 11 days |  |  |  |  |  |
|  |  |  |  |  |  |  | 70°F, 50% RH | 70°F, 80% RH | 120° dry | 120°F, 65% RH |  |  |
| 14 | MA/KF2001/MMA/MAA | 20/25/50/5 | 30 | A | 157 | 71 | 391 | 410 | 403 | 379 |  | 50 |
| 15 | MA/KF2001/MMA/MAA | 45/25/20/5 | 42 | A | 23 | 55 | 30 | - | 79 | 65 |  | 84 |
| 16 | MA/KF2001/MMA/MAA | 55/25/20/5 | 38 | A | 15 | 90 | 88 | 53 | 37 | 78 |  | 88 |
| 17 | MA/KF2001/MMA/MAA | 60/25/20/5 | 36 | A | 37 | 123 | 97 | 82 | 39 | 111 |  | 88 |
| 18 | MA/KF2001/MMA/MAA | 70/25/20/5 | 34 | A | 31 | 90 | 87 | 51 | 171 | 124 |  | 90 |
| 19 | MA/KF2001/MMA/MAA | 70/25/20/5 | 33 | A | 58 | 170 | 117 | 103 | 183 | 172 |  | 85 |
| 20 | MA/KF2001/MMA/MAA | 50/25/20/5 | 40 | B | 27 | 302 | 182 | 215 | 351 | 317 |  | 92 |

A=ACRYLIC
B=RUBBER

Example 21

The composition of Example 21 was prepared in the following manner:

First, a solvent borne sample was prepared by charging a 4 ounce glass bottle with 4 grams of 15K silicone macromer (SiMac), the preparation of which is described in U.S. Patent No. 7,728,571, 16 grams ethyl methacrylate (EMA), 30 grams methyl ethyl ketone (MEK) and 0.06 g 2-2'-azobisbutyronitrile (AIBN). Thereafter, the contents of the bottle was purged with nitrogen gas for two minutes. Then the bottle was sealed and tumbled in a 55°C water bath for 48 hours.

The sample was then diluted to 10% solids for coating. 40 grams of 40% solids polymer solution, 96 grams of toluene and 24 grams of isopropanol (IPA) were added to a 16 ounce wide mouth jar. The mixture was then shaken to form a homogenous mixture. The ingredients utilized in forming a solvent borne solution and the amount of the ingredients utilized are reported in Tables 4 and 5 respectively. The ingredients of the release coating, the weight percentage of the ingredients and the test results are reported in Table 6.

Examples 22-27

The copolymers of Examples 22-27 were prepared in accordance with the procedure outlined in Example 21. The ingredients utilized in forming a solvent borne solution and the amount of the ingredients utilized are reported in Tables 4 and 5 respectively.

TABLE 4

| Example | Ingredients Utilized in Polymerization | Amount of Ingredients Utilized (gms.) |
|---|---|---|
| 21 | 15K SIMAC/EMA/MEK/AIBN | 4/16/30/0.06 |
| 22 | 15K SIMAC/EMA/MMA/MEK/AIBN | 5/7.5/7.5/30/0.06 |
| 23 | 15K SIMAC/EMA/BMA/MEK/AIBN | 5/7.5/7.5/30/0.06 |
| 24 | 15K SIMAC/EMA/MA/MEK/AIBN | 5/7.5/7.5/30/0.06 |
| 25 | 15K SIMAC/MMA/BMA/MEK/AIBN | 5/7.5/7.5/30/0.06 |
| 26 | 15K SIMAC/EMA/ODA/MEK/AIBN | 5/11/4/30/0.06 |
| 27 | 15 K SIMAC/EMA/AA/MEK/AIBN | 5/7.5/7.5/30/0.06 |

TABLE 5

| Example | Ingredients Utilized In Preparation of Solvent-borne dilution | Amount of Ingredients Utilized (gms.) |
|---|---|---|
| 21 | polymer[2]/toluene/IPA | 40/96/24 |
| 22 | polymer/toluene/IPA | 40/96/24 |
| 23 | polymer/toluene/IPA | 40/96/24 |
| 24 | polymer/toluene/IPA | 40/96/24 |
| 25 | polymer/toluene/IPA | 40/96/24 |
| 26 | polymer/toluene/IPA | 40/96/24 |
| 27 | polymer/toluene/IPA | 40/96/24 |

[2] The polymer is the reaction product of the components listed in Table 5 for each example.

Table 6

| Ex. | Ingredients | Wt% Ingredients | Tg °C | Tape | Release g/inch | | % Toner Receptivity |
|---|---|---|---|---|---|---|---|
| | | | | | Initial | 3 days 150°F dry | |
| 21 | EMA/15KSiMac | 80/20 | 47 | A | 34 | - | 88 |
| 22 | EMA/MMA/15KSiMac | 37.5/37.5/25 | 84 | A | 70 | 905 | 88 |
| 23 | EMA/BMA/15KSiMac | 37.5/37.5/25 | 41 | A | 61 | 1235 | 90 |
| 24 | EMA/MA/15KSiMac | 37.5/37.5/25 | 35 | A | 23 | 498 | 87 |
| 25 | MMA/BMA/15KSiMac | 37.5/37.5/25 | 57 | A | 32 | 954 | 88 |
| 26 | EMA/ODA/15KSiMac | 55/20/25 | - | A | 91 | 1191 | 96 |
| 27 | EMA/AA/15KSiMac | 37.5/37.5/25 | 85 | A | 34 | 419 | 99 |

A = acrylic

## COMPARATIVE EXAMPLES 1-5

The samples of Comparative Examples 1-5 comprised commercially available label stock coated with toner receptive materials. The samples were tested in accordance with the procedures outlined above utilizing acrylic tape. The label stock utilized and the test results is reported in Table 7.

Table 7

| | Percentage Toner Receptivity | Release (g/in) |
|---|---|---|
| Ex. | 180° Peel/90" per min. | 70°F/50%RH Immediate (initial) |
| C1[1] | 1.88 | 109 |
| C2[2] | 0.47 | 65 |
| C3[3] | 0.28 | 80 |
| C4[4] | 0.43 | 160 |
| C5[5] | 1.65 | 216 |

[1] Lazer Printer Labels 30-up stock #5160 manufactured by the Avery Commercial Product Division of Avery International Corporation of Azusa, CA.

[2] Lazer Label Z-Label 30-up stock # LP30101 manufactured by Z-Label of Kansas City, MO.

[3] Presaply Laser Printer Labels Dennison 30-up stock # 37-505 manufactured by Dennison Mfg. Company of Framington, MA.

[4] Hewlett Packard 30-up stock # 92157K manufactured by the Hewlett-Packard Company.

[5] Laser/PPC Labels Rayven 30-up stock # BJ05-G manufactured by Rayven, Inc. of St. Paul, MN.

The test results indicate that the release coating of the present invention anchors toner much more effectively than the release coatings utilized in the Comparative Examples. Visually this is seen in a comparison of Figs. 1 and 2 wherein the samples were tested in accordance with the Toner Receptivity Test described above. The asterisk pattern in Fig. 2 was not substantially anchored compared to Applicants' release coating shown in Fig. 1. Applicant's composition utilized in Fig. 1 comprises MA/MAA/MMA/KF2001 in the following amounts 50/5/20/25.

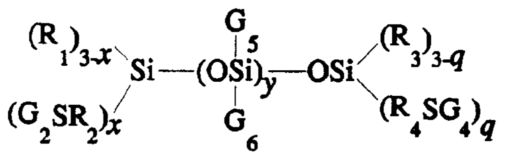
Thus, the coating of the present invention significantly decreases the attendant problems associated with toner particles which are dislocated from release coatings.

In summary, a novel toner receptive release coating is described. Although specific embodiments and examples of the present invention have been described herein, it should be borne in mind that these are by way of explanation and illustration and the present invention is not limited thereby. Certainly, modifications which are within the ordinary skill in the art are considered to lie within the scope of this invention as defined in the following claims including all equivalents.

## Claims

1. A release coating receptive to particles emitted by electrophotoconductive devices comprising a polymer having at least one vinyl polymeric segment having a $T_g$ between -10°C and 65°C and at least one siloxane polymeric segment wherein release coat is capable of substantially anchoring said particles thereto.

2. The release coating of Claim 1 wherein said polymer is a copolymer comprising the formula:



$$\begin{matrix}(R_1)_{3-x}\\(G_2SR_2)_x\end{matrix}\!\!>\!Si-(\underset{G_6}{\overset{G_5}{OSi}})_y-OSi\!<\!\!\begin{matrix}(R_3)_{3-q}\\(R_4SG_4)_q\end{matrix}$$

wherein

$R_1$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_2$ can independently be the same or different and are divalent linking groups;

$R_3$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_4$ can independently be the same or different and are divalent linking groups;

x is an integer of 0-3;

y is an integer of 10 or greater;

q is an integer of 0-3;; and

$G_5$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, fluoralkyl, hydrogen, and -WSA;

A is a vinyl polymeric segment or block consisting essentially of polymerized free radically polymerized monomer;

$G_6$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkoxy, alkylamino, fluoroalkyl, hydrogen and -WSA; and

$G_2$ and $G_4$ are A.

3. The release coating of Claim 1 wherein said polymer is a copolymer of D and E monomers copolymerized to form a polymeric backbone with F monomer grafted thereto wherein:

   D is at least one free radically polymerizable vinyl monomer;

   E is at least one polar monomer copolymerizable with D, the amount of E being up to 30% of the total weight of all monomers, and

   F is a monomer having the general formula

   $X\text{-}(Y)_nSiR_{(3-m)}Z_m$ wherein

   X is a vinyl group copolymerizable with the D and E monomers,

   Y is a divalent linking group where n is zero or 1;

   m is an integer of from 1 to 3;

   R is hydrogen, lower alkyl (e.g., methyl, ethyl, or propyl), aryl (e.g., phenyl or substituted phenyl), or alkoxy; and

   Z is a monovalent siloxane polymeric moiety having a number average molecular weight above about 1,000 and is essentially unreactive under copolymerization conditions.

4. The release coating of Claim 3 wherein said D monomer is selected from the group consisting of styrene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, acrylic or methacrylic acid esters of non-tertiary alcohols and tertiary alcohols having from 1 to about 18 carbon atoms and mixtures thereof.

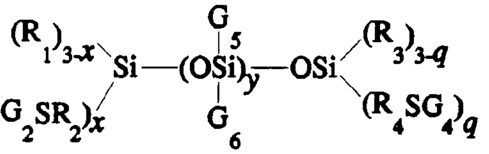
5. The release coating of Claim 3 wherein said E monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, N,N-dimethylacrylamide, methacrylonitrile and maleic anhydride.

6. An image receiving article comprising:

   a. a release coating coated over a portion of a front face of a liner comprising a polymer having at least one vinyl polymeric segment having a $T_g$ between -10°C and 65°C and at least one siloxane polymeric segment wherein said coating is capable of substantially anchoring toner particles emitted by an electrophotoconductive device; and

   b. at least one substrate having a front and a back face, at least a portion of said back face coated with an adhesive wherein said back face of said substrate is secured to said liner.

**7.** The release coating of Claim 6 wherein said polymer is a copolymer comprising having the formula:



$$\begin{array}{c}(R_1)_{3-x}\\(G_2SR_2)_x\end{array}\!\!>\mathrm{Si}-(\mathrm{O}\overset{G_5}{\underset{G_6}{\mathrm{Si}}})_y-\mathrm{OSi}<\!\!\begin{array}{c}(R_3)_{3-q}\\(R_4SG_4)_q\end{array}$$

wherein

$R_1$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_2$ can independently be the same or different and are divalent linking groups;

$R_3$ are monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

$R_4$ can independently be the same or different and are divalent linking groups;

x is an integer of 0-3;

y is an integer of 10 or greater;

q is an integer of 0-3;; and

$G_5$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylamino, fluoralkyl, hydrogen, and -WSA;

A is a vinyl polymeric segment or block consisting essentially of polymerized free radically polymerized monomer;

$G_6$ are monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, alkoxy, alkylamino, fluoroalkyl, hydrogen and -WSA; and

$G_2$ and $G_4$ are A.

**8.** The release coating of Claim 6 wherein said polymer is a copolymer of D and E monomers copolymerized to form a polymeric backbone with F monomer grafted thereto

wherein

D is at least one free radically polymerizable vinyl monomer;

E is at least one polar monomer copolymerizable with D, the amount of E being up to 30% of the total weight of all monomers, and

F is a monomer having the general formula

$X\text{-}(Y)_nSiR_{(3-m)}Z_m$ wherein

X is a vinyl group copolymerizable with the D and E monomers,

Y is a divalent linking group where n is zero or 1;

m is an integer of from 1 to 3;

R is hydrogen, lower alkyl (e.g., methyl, ethyl, or propyl), aryl (e.g., phenyl or substituted phenyl), or alkoxy; and

Z is a monovalent siloxane polymeric moiety having a number average molecular weight above about 1,000 and is essentially unreactive under copolymerization conditions.

**9.** The release coating of Claim 8 wherein said D monomer is selected from the group consisting of styrene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, acrylic or methacrylic acid esters of non-tertiary alcohols having from 1 to about 18 carbon atoms and mixtures thereof.

**10.** The release coating of Claim 8 wherein said E monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, N,N-dimethylacrylamide, methacrylonitrile and maleic anhydride.

**11.** The article of Claim 6 wherein said substrate is a label.

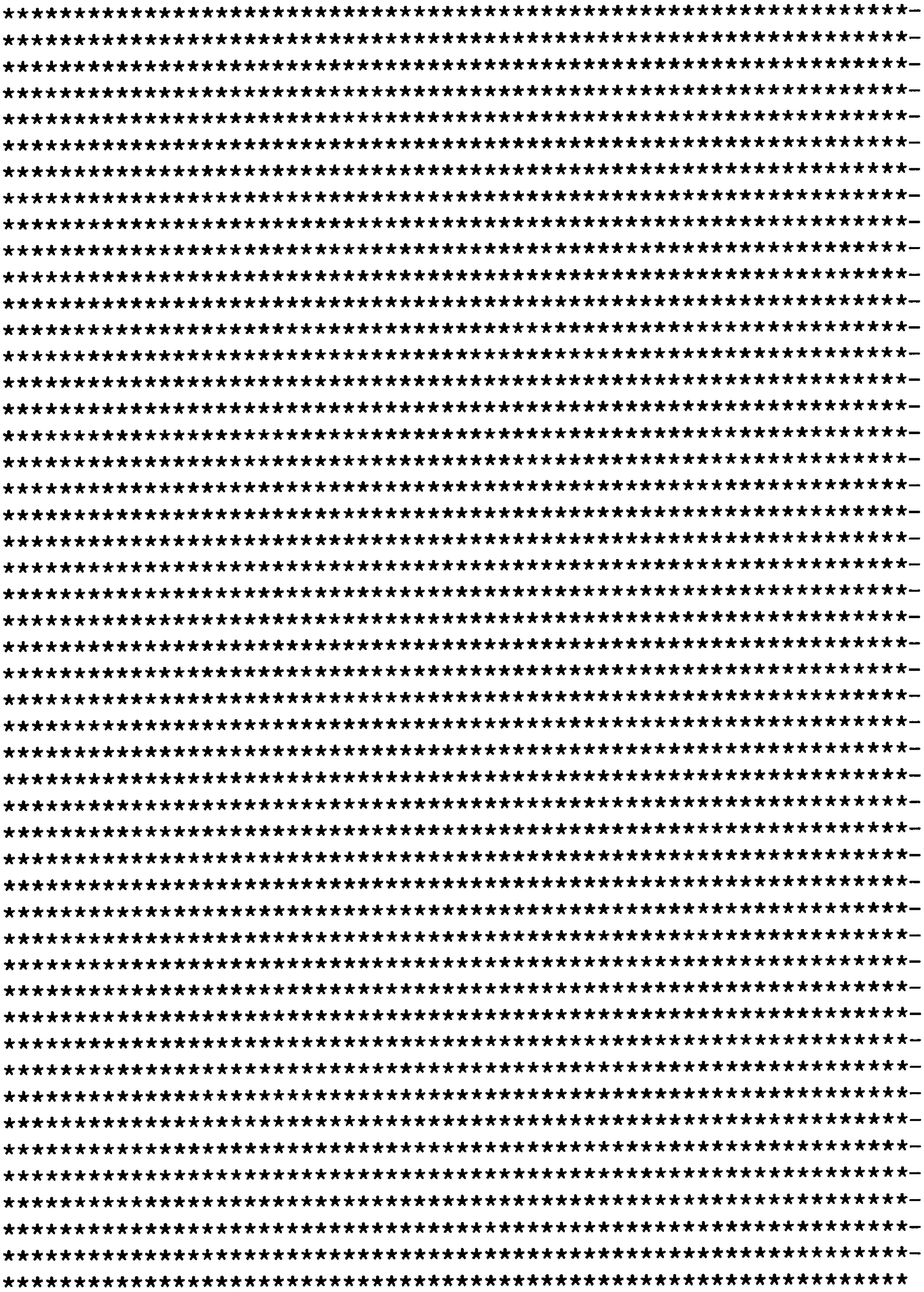


*Fig. 1*

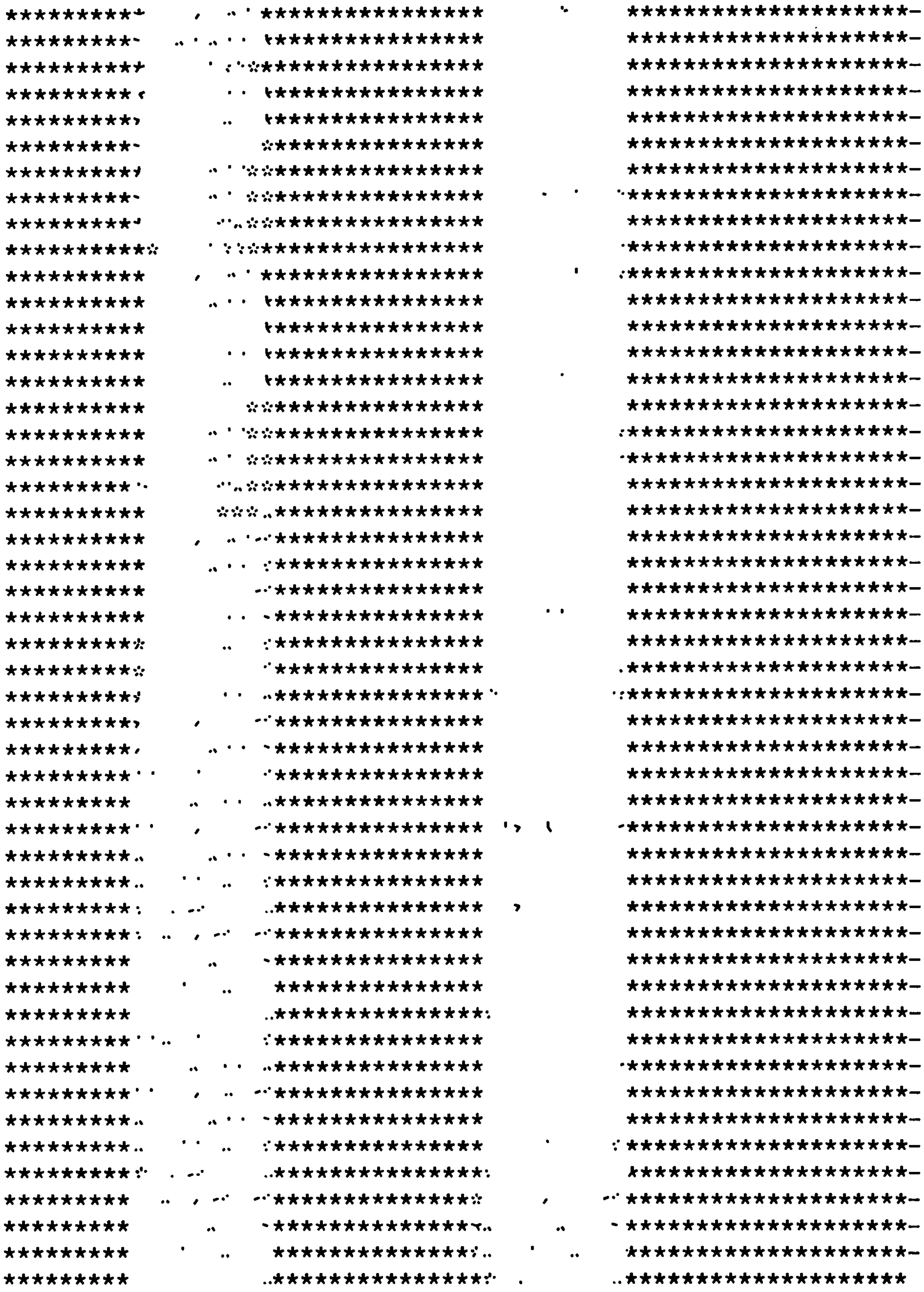


Fig. 2

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 94 40 0679

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.5) |
|---|---|---|---|
| A | US-A-4 942 410 (JOHN J. FITCH, TIM PARKER)<br>* claims 1-12 *<br>--- | 1-11 | G03G7/00 |
| A | EP-A-0 437 073 (MINNESOTA MINING AND MANUFACTURING COMPANY)<br>* page 14, line 10 - page 16, line 18; claims 1-11; table 3 *<br>--- | 1-11 | |
| A | DATABASE WPI<br>Week 8210,<br>Derwent Publications Ltd., London, GB;<br>AN 82-18959E (10)<br>& JP-A-57 019 753 (RICOH K.K.) 2 February 1982<br>* abstract *<br>--- | 1-11 | |
| A | DATABASE WPI<br>Week 7915,<br>Derwent Publications Ltd., London, GB;<br>AN 79-28802B (15)<br>& JP-A-54 030 036 (CANON K.K.) 6 March 1979<br>* abstract *<br>----- | 1-11 | TECHNICAL FIELDS SEARCHED (Int.Cl.5)<br>G03G |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 17 June 1994 | Hindia, E |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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