(1) Publication number:

0 320 533 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87118873.6

(5) Int. Cl.4: G03G 15/20 , G03G 15/16 , G03G 21/00

22 Date of filing: 18.12.87

② Date of publication of application:21.06.89 Bulletin 89/25

Applicant: Toray Silicone Company, Ltd. 8, 2-chome Muro-machi Nihonbashi Chuo-ku Tokyo 103(JP)

Designated Contracting States:
BE DE FR GB

2 Inventor: Shimizu, Koji
25-14, 4-chome, Aobadai
Ichihara-shi Chiba Prefecture(JP)
Inventor: Yoshida, Keiji
6, 1-chome, Yushudai Nishi
Ichihara-shi Chiba Prefecture(JP)

Inventor: Hamada, Mitsuo 5-17, 3-chome, Okubo Kisarazu-shi Chiba Prefecture(JP)

Representative: Spott, Gottfried, Dr. et al Patentanwälte Spott und Puschmann Sendlinger-Tor-Platz 11 D-8000 München 2(DE)

- Roll covered with silicone material and method for producing same.
- This invention provides a silicone elastomer-covered roll consisting essentially of a central roll axle that is in contact with an inner layer of cured silicone elastomer having a hardness value no greater than 30 on the JIS A scale and an outer layer of cured silicone material having a hardness in excess of that of the inner layer. The roll is resistant to assuming a permanent compression set during use, in addition to exhibiting excellent soiling resistance. In particular, when used as a fixing roll in an electrophotographic copier, the contact area with the hard roll can increase, resulting in a clear image on the copy paper.

EP 0 320 !

ROLL COVERED WITH SILICONE MATERIAL AND METHOD FOR PRODUCING SAME

15

This application is a continuation-in-part of copending application Serial No. 095,795 that was filed on September 14. 1987 in the name of the present inventors.

1

This invention relates to a roll covered with a silicone material suitable for the various applications including transfer rolls, heating rolls, pressure rolls and clearing rolls, typically found in electrophotographic copiers and facsimile devices. More particularly this invention relates to such rolls that contain a surface layer of cured silicone material that is harder than the underlying rubber and to a method for producing these rolls.

Contact thermal fixing is widely used. for example in electrophotographic copiers. In contact thermal fixing, an image is electrophotographically formed or the photoreceptor by toner (a thermoplastic resin powder). subsequently transferred to the transfer sheet and then fixed in a fixing element to generate the copy.

Contact thermal fixing employs a device referred to as a heat-fixing roll assembly comprising a hard heated roll, whose surface has both heat resistance and releasibility, and a soft pressure roll, which possesses heat resistance, releasibility, and flexibility. To fix a toner image these two heat-fixing rolls are pressed together at a designed pressure, and the image-carrying transfer paper is passed between the rolls. Under these conditions the soft roll should undergo an increase in contact area while in contact with the hard roll in order to obtain a clear image. A problem encountered with prior art soft rolls is their tendency to assume a permanent set because they are continually being deformed.

With regard to the soft rolls used for paper advance in for example, facsimile devices, soiling of the original occurs as a result of use and accumulation of powder from the paper and other sources, with the result that the quality of the image is adversely affected.

In attempting to solve these problems, rolls have been proposed in which a relatively hard material such as a fluorinated resin or a flexible metal is additionally coated around the outer circumference of a low-hardness rubber.

Japanese Patent Publication No. 20232/80, published on April 19, 1980, discloses a roller comprising a metal core, an under-coat of a specified organosiloxane composition that also includes an allyl ester of a polybasic acid, a metal salt of a fatty acid and an alkoxysilane. and an outer coating of a silicone rubber.

Research Disclosure Nos. 2178,033 and 217.034, published by Kenneth Mason Publica-

tions. Ltd. on April 20, 1982 and U.S. Pat. No. 4,430,406, which issued to J. Newkirk et al. on May 4. 1983 disclose a roller comprising an inner layer of a silicone elastomer and an outer layer of an elastomeric organic fluoropolymer or a fluorosilicone that resists absorption of fuser oil absorbed by the inner layer. An intermediate layer has a composition that changes continuously or in a step-wise manner from that of the inner layer to that of the outer layer.

West German Pat. No. 3,539,377, which issued on May 22, 1986 describes a roller having an elastic silicone rubber layer that is coated with a sintered fluorinated organic resin such as polytetrafluoroethylene.

Japanese Patent Publication No. 26070/61, which was published on February 5, 1986, is directed to a heat fixing roll comprising a layer of silicone rubber sponge and a hard layer formed on the outer surface of the sponge rubber.

U.S. Pat. No. 4,329,565, which issued to Namiki et al. on May 11, 1982, discloses a fixing roll comprising a layer of resilient material that is overlaid with a layer of offset-preventing material containing from 1 to 5 percent of a thermally conductive metal powder. The offset-preventing material can be a silicone, fluorosilicone or organic resin.

Japanese Patent Publication No. 56854/57, which issued on April 5, 1982 discloses a roller formed from a heat hardenable silicone rubber that is coated with a layer of anti-static material prepared by adding a peroxide and either sodium sulfate or a sulfonamide to a heat hardenable silicone rubber.

Canadian Pat. No. 1,116,549, which issued on January 19, 1982 discloses a fuser roll for a copier consisting essentially of a thermally conductive metal tube coated with a thin layer of a cured silicone rubber. The rubber layer exhibits a thickness of about 0.25 mm. and is exposed to ultraviolet radiation under an inert atmosphere following curing.

Japanese Patent Publication No. 38957/61, which was published on August 20, 1987 discloses forming a roller by moiding a silicone rubber on a metal core, inserting the roller into a tube formed from a fluorinated resin and heating the resultant composite to shrink the resin tube on to the silicone rubber layer.

Japanese Patent Publication No. 28213, which issued on February 6, 1987, discloses a method for forming a copier roll by placing a heat-resistant resin tube and a central core in a mold, pouring in a heat resistant material such as a curable silicone

rubber composition between the tube and the core to form an intermediate layer that is then vulcanized to form an elastomer.

Japanese Patent Publication No. 26027/87, which was published on June 5, 1987 discloses a fixing roll comprising a metal roll, an inner layer of a silicone rubber and an outer layer of a fluorosilicone rubber.

U.S. Pat. No. 4,149,797, which issued to G. Imperial on April 17, 1979 and U.S. Pat. No. 4,083,092, which issued to Imperiale et al. on April 11, 1978 disclose a fixing roll comprising a rigid core, an organic rubber layer adhered to the core and an outer protective sleeve. The sleeve has a high flex life and blocks air from reaching and oxidizing the rubber.

Soft rolls known in the art, including the silicone rubber-covered rolls, suffer from the problems of

- 1) not increasing in contact area along the line of contact between the soft roll and the aforementioned hard roll
- 2) and assuming a permanent compression set. As a result, there is a strong tendency for the copy image to be unclear.

The present inventors carefully studied methods for eliminating these problems, and developed the present invention as a consequence.

An objective of the present invention is to provide a soft roll coated will a silicone material which is not subject to permanent set during use and which has an excellent resistance to soiling. This invention also provides a method for preparing these rolls.

A particular object of the present invention is to provide a soft roll whose contact area with an adjacent hard roll can expand along the line of contact with a hard roll. This provides a clear copy image when the rubber-covered roll is used as a fixer roll in an electrophotographic device.

Another objective is to provide a method for the production of these soft rolls.

The aforementioned objectives can be achieved by a roll wherein a first layer of cured silicone material having a hardness no greater than 30 on the JIS A scale is formed on a roll axle and covered with a second layer of cured silicone material having a hardness greater than that of first layer.

This invention provides a roll coated with silicone material, said roll comprising a roll axle coated with an inner layer of elastomeric cured silicone material having a hardness value of no greater than 30 on the Japanese Industrial Standards (JIS) A scale, where the lower surface of said layer is in contact with said axle and the upper surface of said layer is in contact with an outer layer of a cured

silicone material having a hardness greater than that of said inner layer.

The present invention also provides a preferred method for preparing the present silicone-covered roll. In accordance with this method an organopolysiloxane having at least 3 silicon-bonded hydrogen atoms in each molecule is applied to the interior surface of a mold. A roll axle is then introduced into the interior of this mold, followed by introduction of a liquid silicone composition that is convertible to the aforementioned elastomeric cured material having a hardness no greater than 30 on the JIS A scale. As the final step the organopolysiloxane and liquid silicone rubber composition are thermally cured.

No specific restrictions apply to the roll axle used in the present invention. The axle is formed from a metal typically used as a roll core metal. The surface of the axle can be treated with an anticorrosive agent or a primer.

The inner layer of the present roll is adjacent to the roll axle and consists essentially of an elastomeric cured silicone material having a hardness no greater than 30 on the JIS A scale. This material is obtained from an organopolysiloxane-based composition that cures either at room temperature or upon heating. The cured silicone material is not specifically restricted, and includes silicone gels and conventional silicone rubbers. The hardness of the cured material must be no greater than 30 on the JIS A scale, measured as specified in JIS C 2123. The hardness of the cured silicone material is preferably no more than 20, and most preferably no more than 10.

If the hardness value of the inner layer exceeds 30 on the JIS A scale the roll will not exhibit the advantages of the present invention.

The thickness of the inner layer is not specifically restricted, and will depend upon the end use application of the roll.

An outer layer of cured silicone material having a hardness in excess of that of the aforementioned inner layer of cured silicone material is the characterizing feature of the present rolls. The principal component of the cured surface layer is at least one organopolysiloxane. Preferably the organopolysiloxanes present in the inner and outer layers are identical.

No specific restrictions apply to the outer layer other than the fact that a tacky semi-cured material or cured gel material is undesirable. Concrete examples of cured materials suitable for use as the outer layer are silicone rubbers and silicone resins.

The cured outer layer must be harder than the cured inner layer. A harness value in the range of 35 to 90 on the JIS A scale is preferred for the outer layer. When the hardness of the outer layer is less than that of the cured inner layer, the roll will

55

30

have a tacky surface, and will not exhibit the desired resistance to soiling and development of a permanent compression set.

The cured outer layer preferably has a thickness of approximately 1/10 to 1/1000 that of aforementioned inner layer. The thickness of the outer layer is preferably no greater than 1,000 microns.

The mold used to manufacture the siliconecovered roll in accordance with the present method can be formed from metal, silicone rubber, or a synthetic resin such as a polyester or nylon. These materials are typically used as mold materials for silicone rubber compositions.

No specific restriction apply to the mold so long as the curable liquid silicone rubber composition can flow into the mold and be subsequently cured.

In accordance with a preferred method for preparing the present roll an organopolysiloxane containing at least 3 silicon bonded hydrogen atoms is applied to the interior surface of the mold, the roll axle is placed in the center of the mold cavity and the cavity is subsequently filled with a curable liquid silicone composition that will form the inner layer of the roll upon curing. The organopolysiloxane is in contact with and cures together with the curable liquid silicone composition during molding to form the hard outer layer of the roll. Although this organopolysiloxane must have at least 3 silicon-bonded hydrogen atoms in each molecule, it can be used in combination with an organopolysiloxane having 2 silicon-tonded hydrogen atoms in each molecule to vary the hardness of the outer layer.

The molecular structure of the organopolysiloxane containing at least three silicon-bonded hydrogen atoms per molecule is not specifically restricted. The molecular structure of this molecule may be straight chain, branch-containing straight chain, or cyclic. When a harder and tougher outer layer must be formed at the surface of the siliconecovered roll, it is preferable to use a branched organopolysiloxane, for example, a copolymer composed of (CH₃)₂HSiO_{1/2} and SiO_{4/2} units, or a copolymer of (CH₃)₃SiO_{1/2}, (CH₃)₂HSiO_{1/2}, and SiO_{4/2} units. Non-limiting examples of the organopolysiloxane ingredient include but are not trimethylsiloxy-terminated limited to hydrogenpolysiloxanes, trimethylsiloxy-terminated dimethylsiloxane-methylhydrogensiloxane copolymers. dimethylhydrogensiloxy-terminated dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylsiloxane-methylhydrogensiloxane cyclic copolymers, copolymers composed of (CH₃)₂HSiO_{1/2} and SiO_{4/2} units, and copolymers composed of (CH₃)₃SiO_{1/2}, (CH₃)₂HSiO_{1/2}, and SiO_{4/2} units.

The organopolysiloxane can be applied to the

inner surface of the mold by any of the known conventional means, including spraying, brushing and sponge coating. No specific restriction apply to quantity of organopolysiloxane, applied to the inner mold surface, as long as a continuous, dry film is formed on the mold surface.

The curable liquid silicone composition that forms the inner elastomer layer of the present roll can be a liquid or paste at room temperature. and is based on a reactive group-containing liquid organopolysiloxane, a crosslinker and/or a curing catalyst. The composition is capable of curing into a rubbery elastomer or gel at room temperature or with heating. It can be of the "sag" or "non-sag" type.

The curing mechanism of this composition is not critical, and can be an addition-reaction mechanism, organoperoxide-based radical reaction-curing mechanism, or condensation-reaction mechanism. Compositions that cure by means of an addition reaction are preferred in order to obtain a faster and more uniform curing. Particularly preferred addition-curable liquid silicone compositions for use in preparing the inner elastomer layer comprise (A) an organopolysiloxane having at least 2 lower alkenyl groups in each molecule; (B) an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity such that the molar ratio of the total quantity of silicon-bonded hydrogen atoms in the present component to the total quantity of all lower alkenyl groups in component (A) is from 0.1 to 1; and (C) a concentration of a platinum-type catalyst equivalent to from 0.1 to 1,000 weight parts platinum metal for each one million weight parts of the total of components (A) and (B).

Component (A) of the preferred curable compositions is the principal component of the composition. Curing of the composition proceeds by the addition reaction of component (A) with component (B) under the catalytic activity of component (C). Component (A) must contain at least 2 siliconbonded lower alkenyl radicals in each molecule. These lower alkenyl radicals are exemplified by vinyl, allyl, and propenyl.

The alkenyl radicals of ingredient (A) can be present at any location in the molecule, but are preferably present at least at the molecular terminals. The molecular configuration of this component can be straight chain, branch-containing straight chain, cyclic, or network, but is preferably straight chain, possibly slightly branched. No specific restriction applies to the molecular weight of this component. Also, while the viscosity may range from that of low-viscosity liquids to very high-viscosity gums and thus is not specifically restricted, the viscosity at 25°C is preferably at least 100 centipoise (0.1 Pa.s) in order to obtain a

15

20

30

35

cured material in the form of a rubbery elastomer. alkenyl-substituted of this Examples ganopolysiloxane include but are not limited to methylvinylpolysiloxanes, methylvinylsiloxanedimethylsiloxane copolymers, dimethylvinylsiloxydimethylpolysiloxanes, terminated dimethylvinylsiloxy-terminated dimethylsiloxane-methylphenylsiloxane copolymers, dimethylvinylsiloxy-terminated dimethylsiloxane-diphenylsiloxanemethylvinylsiloxane copolymers, trimethylsiloxy-terminated dimethylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxy-terminated dimethylsiloxane-methylphenylsiloxanecopolymers, methylvinylsiloxane dimethylvinylsiloxy-terminated methyl(3,3,3-trifluoropropyl)polysiloxanes, dimethylvinylsiloxy-terminated dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers, and polysiloxanes consisting essentially of $CH_2 = CH(CH_3)_2SiO_{1/2}$, $(CH_3)_3SiO_{1/2}$, and SiO4/2 units. Combinations of the above organopolysiloxanes can also be used in the present invention.

Component (B) of the preferred compositions for preparing the inner elastomer layer of the present rolls is a crosslinker for component (A). Curing proceeds by the addition of the siliconbonded hydrogen atoms in this component with the lower alkenyl groups in component (A) under the catalytic activity of component (C). This componen (B) must contain at least 2 silicon-bonded hydrogen atoms in each molecule in order to function as a crosslinker.

The molecular structure of component (B) is not specifically restricted, and can be straight chain, branch-containing straight chain, or cyclic. The molecular weight of this component is likewise not specifically restricted, however the viscosity of this component, measured at 25° C., is preferably 1 to 50,000 centipoise (0.001 to 50 Pa.s) in order to obtain good miscibility with component (A).

The concentration of component (B) is preferably one that will provide a molar ratio of silicontonded hydrogen atoms to all lower alkenyl radicals in component (A) of from 0.1 to 1. Most preferably this ratio is from 0.4 to 0.6. The crosslinking density will be too low at molar ratios below 0.1, resulting in unsatisfactory curing. On the other hand, the crosslinking density of the cured inner layer will be too high when the molar ratio silicontonded hydrogen atoms to total alkenyl radicals exceeds 1, and it will be difficult to form a hard covering layer at the surface of the silicone-covered roll.

It will be understood that when the curable composition used to form the inner elastomer layer

includes an additional organopolysiloxane containing a large concentration of alkenyl radicals for the purpose of providing reinforcement or other properties to the cured elastomer, the amount of organopoly-siloxane containing silicon-bonded hydrogen atoms is preferably sufficient to reacts with these additional alkenyl radicals.

Examples of component (B) include but are not limited to trimethylsiloxy-terminated methylhydrogenpolysiloxanes, trimethylsiloxy-terminated dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylhydrogensiloxy-terminated dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylsiloxane-methylhydrogensiloxane cyclic copolymers, copolymers composed of (CH₃)₂HSiO_{1/2} and SiO_{4/2} units, and copolymers composed of (CH₃)₃SiO_{1/2}, (CH₃)₂HSiO_{1/2}, and SiO_{4/2} units.

Component (C) of the preferred curable compositions is a catalyst for the addition reaction of silicon-bonded hydrogen atoms with alkenyl radicals. Non-limiting examples of this component include chloroplatinic acid, including solutions of this catalyst in alcohol or ketone and these solution following aging, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, chloroplatinic acid-diketone complexes, platinum black, and platinum supported on a carrier.

Component (C) is present in an amount equivalent to from 0.1 to 1,000 weight parts of platinum-group metal for each one million parts by weight (ppm) of the total quantity of components (A) and (B). The crosslinking reaction will not proceed satisfactorily at below 0.1 ppm. while exceeding 1,000 weight parts is uneconomical. In the typical case, the preferred catalyst concentration is equivalent to approximately 1 to 100 ppm of platinum-group metal.

The curable liquid silicone compositions used to form the inner layer of the present roller can include at least one filler to adjust the fluidity and/or improve the mechanical strength of the molded article. These fillers are exemplified by reinforcing fillers such as precipitated silica, fumed silica, calcined silica, and fumed titanium dioxide, and by non-reinforcing fillers such as quartz powder, diatomaceous earth. asbestos, aluminosilicic acid, iron oxide, zinc oxide, and calcium carbonate. The surface of the filler can optionally be treated with an organosilicon compound, for example, hexamethyldisilazane, trimethylohlorosilane, or a hydroxyl terminated polydimethylsiloxane.

The present curable liquid silicone compositions can also include small or very small amounts of inhibitors for the curing reaction, so long as these inhibitors do not adversely affect the objectives of the present invention. Non-limiting exam-

25

35

40

50

55

ples of such inhibitors include acetylenic compounds, hydrazines, triazoles, phosphines, and mercaptans.

Other optional ingredients that can be present in the curable precursor of the elastomeric inner layer include but are not limited to pigments, heat stabilizers, flame retardants, plasticizers, and organopolysiloxane having 1 alkenyl radical in each molecule that are added to reduce the modulus of the cured elastomeric inner layer.

A second class of preferred curable liquid organosiloxane compositions cure by means of a free radical reaction and include an organoperoxide as the curing agent. These compositions include a vinyl group-containing diorganopolysiloxane that is liquid at room temperature and a catalytic quantity of organoperoxide. Optional ingredients include but are not limited to inorganic fillers such as fumed silica and precipitated silica, heat stabilizers, and pigments. The organoperoxide preferably has a decomposition temperature in the range of +25 to +100° C.

Compression molding, transfer molding, and injection molding are typically used to mold liquid silicone rubber compositions, and can be used to introduce the present curable liquid silicone rubber compositions into the interior of the mold and thermally cure them.

When the temperature used to cure the curable liquid silicone material is too low, the curing rate will be reduced and the productivity will be low. On the other hand, when the molding temperature is too high, the resulting silicone elastomer molding will stick to the interior surface of the mold, thus generating problems in de-molding. As a consequence, the molding temperature should be within the range of from 50 to 220°C and preferably in the range of 50 to 170°C.

The silicone-covered roll of the present invention finds use in various applications, for example, as the transfer rolls, fixing rolls, or cleaning rolls used in electrophoto-graphic copiers, and as paperadvance rolls in facsimile devices.

The following examples describe preferred embodiments of the present rolls, and should not be interpreted as limiting the scope of the invention as defined in the accompanying claims. Unless otherwise specified all parts and percentages are by weight and viscosities were measured at 25 °C.

Example 1

100 Parts of a dimethylvinylsiloxy-terminated dimethylpolysiloxane having a viscosity of 2000 centipoise (2 Pa.s) and a vinyl content of 0.23 wt%, 25 parts dry-method silica having a specific surface area of 200 square meters per gram, and 0.5 parts

trimethylsiloxy-terminated methylhydrogen-polysiloxane having a viscosity of 10 centipoise (0.01 Pa.s) and a SiH silicon-bonded hydrogen content of 0.9% were blended to homogeniety to provide a mixture having a viscosity of 5,000 poise (500 Pa.s) at a shear rate of 10 sec⁻¹. A curable liquid silicone composition of this invention was obtained by blending this mixing together with 0.1 part of a solution of chloroplatinic acid in isopropanol. The solution contained 3 percent of platinum.

A metal mold designed for the molding of silicone elastomer-covered rolls and having a chromium-plated interior surface was coated on its interior surface with a trimethylsiloxy-terminated methylhydrogenpolysiloxane having a viscosity of 10 centistokes (10⁻⁵ m²/sec) and a silicon bonded hydrogen atom content of 1.0 wt% to yield a uniform coating density of 0.2 g per square meter.

A cylindrical iron roll axle was also prepared, and coated with a primer consisting essentially of an organopolysiloxane gum, an organopolysiloxane resin, ethyl silicate, a methylhydrogenpolysiloxane, and an organotitanate ester. The primer was applied to the surface of the roll and subsequently cured.

The primed roll axle was mounted inside the aforementioned metal mold, and the liquid silicone composition prepared as described in the preceding portion of this example was then injected into the cavity and thermally cured at 150°C for 10 minutes. After cooling, the obtained silicone-covered roll was removed and the interior portion of the coating was exposed by cutting into the coating using a knife.

The hardness of the interior and exterior layers of the roll coating was then measured using the JIS A scale with the following results: surface layer hardness = 50, inner layer hardness = 10. The thickness of the outer layer was 0.5 mm.

The resiliency of the rubber layer was 10% and the permanent compression set was 15%. The compression set value was obtained by compressing the rubber layer to 75% of its initial thickness for a period of 72 hours while heating the roll at a temperature of 180° C.

When this silicone elastomer-covered roll was used as the pressure roll in the fixing rolls of an electrophotographic copier, the copy paper was not creased, and the copied image was clear.

Example 2

100 Parts of a dimethylvinylsiloxy-terminated dimethylpolysiloxane having a viscosity of 2000 centipoise (2 Pa.s) and a vinyl content of 0.23 wt%, 20 parts dry-method silica having a specific surface area of 200 square meters per gram. 0.4 parts

30

40

45

50

methylhydrogentrimethylsiloxy-terminated polysiloxane having a SiH content of 1.0 wt%, and 0.1 part of a solution of chloroplatinic acid solution in isopropanol (platinum content = 3 percent) were blended to homogeniety to produce a curable liquid silicone composition of this invention. The same methylhydrogenpolysiloxane described in the preceding Example 1 was sprayed on the interior surface of an metal injection mold. The mold was heated to a temperature of 120°C at which time an iron roll core was mounted in the interior of the mold, and the liquid silicone composition prepared as above was then injected and cured. The hardness values of the exterior and interior layers of the resultant silicone elastomer-covered roll of this invention were measured as described in the preceding Example 1, and were 38 and 3, respectively, measured using the JIS A scale. When this roll was used as a paper-advance roll in a facsimile device neither the roll surface nor the image were soiled.

Example 3

100 Parts of a dimethylvinylsiloxy-terminated dimethylpolysiloxane having a viscosity of 2000 centipoise (2 Pa.s) and a vinyl content of 0.23 wt%, 15 parts of carbon black having a specific surface area of 70 square meters per gram (available as Denka Black from Denki Kagaku Kogyo Kabushiki Kaisha) and 0.4 parts of a trimethylsiloxy-terminated methylhydrogenpolysiloxane having a viscosity of 10 centipoise (0.01 Pa.s) and a silicon-bonded hydrogen atom content of 1.0 wt% were blended to homogeniety of yield a mixture having a viscosity of 800 poise (80 Pa.s) at a shear rate of 100 sec-1. To this mixture was added 0.1 part of the chloroplatinic acid solution described in the preceding Example 1 to produce a curable liquid silicone rubber composition of this invention.

A cylindrical metal mold having a chromiumplated inner surface was coated with a cylindrical preformed polyester film and a 10% solution in toluene of a trimethylsiloxy-terminated methylhydrogenpolysiloxane exhibiting a viscosity of 10 centistokes (1×10⁻⁵ m²/sec) and containing 1 percent of silicon- bonded hydrogen was sprayed on the exposed surface of the film to produce a coating density of 5 grams per square meter. The coating was then dried. An aluminum roll axle was then inserted into the cavity's interior, and the liquid silicone rubber composition prepared as described in the preceding portion of this Example was then injected and thermally cured at 130°C for 5 minutes. The resulting molding was a siliconecovered roll having an inner gel layer (hardness = 5) and a 0.4 mm-thick hard covering layer at the surface. This silicone elastomer-covered roll of this invention was used as the pressure roll in the fixing rolls of an electrophotographic copier. No permanent compression set in the roll was observed, and the copied image was clear.

Claims

- 1. A roll covered with silicone material, said roll comprising a roll axle coated with an inner layer of elastomeric cured silicone material having a hardness value of no greater than 30 on the Japanese Industrial Standards (JIS) A scale, where the lower surface of said layer is in contact with said axle and the upper surface of said layer is in contact with an outer layer of a cured silicone material exhibiting a hardness greater than that of said inner layer.
- 2. A roll according to claim 1, where said roll is produced by coating the interior surface of a mold with an organopolysiloxane having at least 3 silicon-bonded hydrogen atoms in each molecule, mounting said roll axle in said mold, introducing into said mold a curable liquid silicone rubber composition that will yield said silicone material having a hardness value of no greater than 30 on the JIS A scale and curing said organopolysiloxane and said liquid silicone rubber composition by heating.
- 3. A roll according to claim 2 wherein the liquid silicone rubber composition comprises
- (A) an organopolysiloxane containing at least 2 silicon-bonded lower alkenyl radicals in each molecule:
- (B) an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, in a quantity such that the molar ratio of the total quantity of silicon-bonded hydrogen atoms in the present component to the total quantity of all lower alkenyl groups in component (A) is from 0.1 to 1; and
- (C) a platinum-type catalyst in an amount equivalent to from 0.1 to 1,000 parts by weight of platinum metal for each one million parts by weight of the total of components (A) and (B).
- 4. A roll according to claim 3 where said lower alkenyl radical is vinyl and said organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule is a polymethylhydrogensiloxane.
- 5. A roll according to claim 4 where said vinyl radicals are present in a dimethylvinylsiloxy-terminated polydimethylsiloxane.



EUROPEAN SEARCH REPORT

EP 87 11 8873

Category	Citation of document with of relevant p	indication, where appropriate, assages	Relevant to claim	CLASSIFICATION OF TH APPLICATION (Int. Cl.4)
X	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 68 (P-553)[2515], 28th February 1987; & JP-A-61 231 578 (SHARP CORP.) 15-10-1986 * Abstract *		1	G 03 G 15/20 G 03 G 15/16 G 03 G 21/00
Y	PATENT ABSTRACTS OF 9 (P-534)[2456], 10 JP-A-61 185 775 (NI 19-08-1986 * Abstract *	JAPAN, vol. 11, no. Oth January 1987; & TTTO KOGYO K.K.)	1	
Y	9 (P-534)[2456], 10	F JAPAN, vol. 11, no. Oth January 1987; & ONISHIROKU PHOTO IND.	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 60 (P-262)[1497], 22nd March 1984; & JP-A-58 209 768 (SHOWA DENSEN DENRAN K.K.) 06-12-1983		2 -	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A		F JAPAN, vol. 10, no. 5th December 1986; & DSHIBA SILICONE CO.	2	G 03 G 15/00 G 03 G 21/00
	The present search report has	•		
THI	Place of search E HAGUE	Date of completion of the search 26-07-1988	search Examiner HILTNER	
X: par Y: par doc A: tec O: no	CATEGORY OF CITED DOCUMI rticularly relevant if taken alone rticularly relevant if combined with an cument of the same category hnological background n-written disclosure ermediate document	E: earlier patent d after the filing nother D: document cited L: document cited	ocument, but pui date in the application for other reason	blished on, or on s