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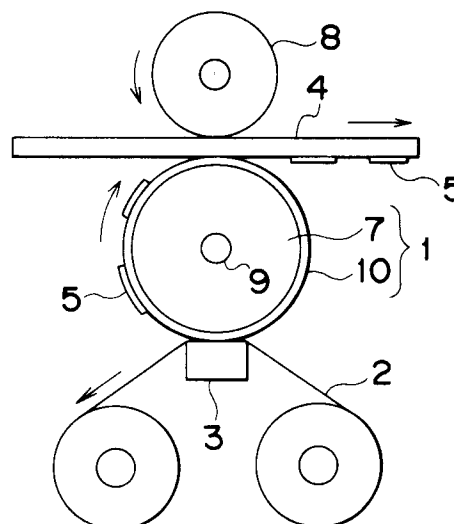
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D-28195 Bremen (DE)(54) **Intermediate recording medium suited for thermal transfer printing.**

(57) An intermediate recording medium (1) is suited for thermal transfer printing of the type wherein after a colored material (5, 5') held on a transfer medium (2, 2') has been transferred onto the intermediate recording medium (1) by a recording head (3), the colored material (5, 5') on the intermediate recording medium (1) is transferred onto and fixed on an image receiving medium (4). The intermediate recording medium (1) is made up of a metallic drum (7) and a silicone rubber layer (10) overlaid on the metallic drum (7) and having a thickness of 1 mm or smaller and a density of 0.90 to 1.15. When a reagent having a surface tension of 45 dyn/cm or greater is placed on the silicone rubber layer (10), the contact angle between the silicone rubber layer (10) and the reagent has a cosine of 0.4 or smaller.

Fig. 1

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to the art of thermal transfer printing. Specifically, the present invention relates to an intermediate recording medium for temporarily recording thereon a colored material and subsequently transferring the colored material onto a recording sheet such as, for example, a standard paper or a bond paper, at a high speed to accomplish a high-quality image duplication.

Description of the Prior Art

The thermal transfer printing technique has been known wherein an ink on a support base is fused by a thermal head for transfer from the support base onto an image receiving medium such as, for example, a paper for recording thereof.

Recently, a new printing technique has been reported wherein the ink is initially transferred onto an intermediate recording medium, for example, a drum or a belt, having a surface layer made of silicone rubber or the like. Ink deposits so transferred onto the intermediate recording medium are subsequently transferred on a paper or the like. The background of this new printing technique is that, with the conventional thermal transfer printing technique with no intermediate recording medium employed, it has been recognized very difficult to accomplish a high-quality printing substantially free from any void occurring in permanently fixed ink deposits on a recording paper.

Homogeneity or flexibility of the silicone rubbers contributes to the homogeneous recording, and the flexibility of the silicone rubber enables the ink deposits recorded on the rubber layer to be transferred and fixed on the paper along surface irregularities of the paper. Such silicone rubber is generally prepared so as to have a hardness of from 30 to 50 by adding an inorganic filler, for example silica, to a material obtained by copolymerizing and cross-linking dimethyl silicone and methylvinyl silicone.

The thermal transfer printing with the use of the above-described intermediate recording medium having a surface layer made of silicone rubber enables high-quality recording on a standard paper or the like. In general, the intermediate recording medium in the form of, for example, a drum is required to have ink receptivity required for receiving an inked image during recording and ink separability or releasability required for transfer of the imaged image onto, for example, a paper. However, the continuous use of the intermediate recording medium having the surface layer made of

silicone rubber deteriorates the ink releasability of the rubber surface thereof. Because of this, the inked image recorded on the intermediate recording medium cannot completely be transferred onto the image receiving medium and the ink deposits are accumulated on the rubber surface, thereby deteriorating the image quality. It is conceivable that the deterioration in ink releasability is attributable to the enlarged surface roughness caused by sliding movement between the paper and the intermediate recording medium. When the ink releasability is imparted by internally adding a liquid such as, for example, a silicone oil to the rubber, such deterioration may conceivably be caused by a reduction in oil quantity within the rubber due to the transfer of the silicone oil to the paper.

SUMMARY OF THE INVENTION

The present invention has been developed to overcome the above-described disadvantages.

It is accordingly an object of the present invention to provide an improved intermediate recording medium capable of temporarily recording thereon a colored material and of subsequently transferring the colored material onto an image receiving medium without lowering the image quality.

The intermediate recording medium according to the present invention is particularly suited for thermal transfer printing of the type wherein after a colored material held on a transfer medium has been transferred onto the intermediate recording medium by a recording head, the colored material on the intermediate recording medium is transferred onto and fixed on an image receiving medium. The colored material may be a resin layer held on the transfer medium for holding thereon the colored material.

In accomplishing the above and other objects, the intermediate recording medium according to the present invention comprises a metallic drum and a silicone rubber layer overlaid on the metallic drum and having a thickness of 1 mm or smaller and a density of 0.90 to 1.15. When a reagent having a surface tension of 45 dyn/cm or greater is placed on the silicone rubber layer, the contact angle between the silicone rubber layer and the reagent has a cosine of 0.4 or smaller.

Preferably, the silicone rubber layer contains a solid release agent at a temperature below 100°C.

Conveniently, the silicone rubber layer contains thermoplastic or thermosetting polymeric components having a colored material releasability by which the colored material is released from the silicone rubber layer.

Advantageously, liquid components or low-molecular components contained in the silicone rubber layer are removed by solvent-extraction. The sili-

cone rubber layer may contain fluid components and an additive which is solidified at temperatures below 100 °C.

The resin layer for holding the colored material is dyed by diffusion or vaporization of a dye contained in the colored material.

According to the present invention, because the intermediate recording medium has a surface layer made of homogeneous and flexible silicone rubber, the surface layer can temporarily receive the colored material transferred from the transfer medium and can subsequently completely transfer it onto the image receiving medium so that the entire colored material may be fixed on the image receiving medium. Even if the intermediate recording medium is continuously used, no transfer residue is left on the intermediate recording medium. The reason for this is that the surface layer has an appropriate colored material releasability which changes little even by the continuous use of the intermediate recording medium. Because of this, the surface layer is so chosen as to have a small roughness, a small surface energy (contact angle), a high density, or the like. According to the present invention, the density of the surface layer is increased not by the use of an inorganic additive, but by increasing the cross-linking density of a rubber material. The increase of the cross-linking density is particularly important. By doing so, during recording, thermally fused colored material is temporarily held only on the surface layer without permeating the inside of the rubber, and the colored material is entirely transferred onto the image receiving medium.

Furthermore, the appropriate thickness of the surface layer provides reliable recording even in the presence of warping or distortions of the recording head. Even if the image receiving medium is a bond paper or the like having a relatively large surface roughness, deposits of the colored material are steadily fixed on the image receiving medium along irregularities of the surface thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become more apparent from the following description of preferred embodiments thereof with reference to the accompanying drawings, throughout which like parts are designated by like reference numerals, and wherein:

Fig. 1 is a schematic elevational view of a thermal transfer printing apparatus employing an intermediate recording medium according to the present invention;

Fig. 2 is a view similar to Fig. 1, but indicating another thermal transfer printing apparatus; and

Fig. 3 is a graph indicating a characteristic of a surface rubber layer of the intermediate recording medium according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, there is schematically shown in Fig. 1 a thermal transfer printing apparatus employing therein an intermediate recording medium 1 according to the present invention.

The recording medium 1 is suited for thermal transfer printing and comprises a metallic drum or roll 7 made of, for example, aluminum and a thin silicone rubber layer 10 overlaid thereon. The drum 7 is internally provided with a heater 9 for heating the recording medium 1. The surface temperature of the recording medium 1 is occasionally maintained generally constant by the heater 9 according to the kind of ink sheets or ribbons. In Fig. 1, reference numerals 2, 3, and 4 denote a hot-melt ink sheet, a recording head such as, for example, a thermal head, and an image receiving medium such as, for example, a standard paper or a bond paper, respectively.

When the apparatus shown in Fig. 1 is in operation, a colored material 5 of the ink sheet 2 is initially thermally transferred on the rubber layer 10 by the recording head 3. The colored material 5 on the rubber layer 10 is subsequently transferred on the image receiving medium 4 passing between the drum 7 and a fixing roll 8 and is fixed by the fixing roll 8. Because the rubber layer 10 is homogeneous, an image formed on the image receiving medium is also homogeneous. Furthermore, because the rubber layer 10 has flexibility and ink separability or releasability, duplicates produced are substantially free from any void which may occur in ink deposits formed along irregularities of fibers of a paper, and also, images formed on the duplicates are superior in fixing or anchoring characteristic.

The preferred hardness (Shore hardness) of the rubber layer 10 ranges from 20 to 60. In order for the colored material to be transferred on and fixed along the fibers of the paper, a hardness of 40 or lower is particularly preferable. The rubber thickness is preferably not greater than 1 mm in order to reduce the effective fixing load, and in this case, a desired image can be fixed even on a bond paper having a Bekk smoothness of 3 seconds or lower by the application of a fixing load of about 20 Kg·f, if the width of the paper is generally equal to that of A4. If the rubber thickness exceeds 1 mm, the fixing load becomes so large as to make it difficult to assemble a printing apparatus that meets this increased fixing load. If the surface

temperature of the rubber layer 10 is maintained at about 70 °C by the heater 9, the fixing characteristic of the image is further enhanced. The preferred lower limit of the rubber thickness is 0.2 mm. The rubber thickness of 0.2 mm or greater can absorb warping or distortions of the thermal head which generally falls within the range of 0.1 mm, thereby enabling homogeneous recording. However, in applications where a so-called shuttle-type thermal head is employed, the lower limit of the rubber thickness may be about 0.01 mm.

The rubber layer 10 must have such a surface property that the outer peripheral surface thereof has an ink receptivity required to receive and retain thereon ink deposits transferred from the ink sheet and, also, a consistent releasability by which the ink deposits can separate away from the surface of the rubber layer 10. Because of this, the surface roughness of the rubber layer 10 is preferably not greater than 20 microns and, more preferably, not greater than 5 microns. A mirror surface having a surface roughness of about 0.1 micron is most preferable. The rubber layer 10 may be molded by the use of a mold, the surface of which is uniformly finished by plating or the like.

In order to chemically enhance the ink releasability, the surface energy should preferably be reduced by enhancing the density of a methyl group on the surface of the rubber layer 10. When a reagent has a surface tension of 45 dyn/cm or greater, the cosine of the contact angle between the rubber layer 10 and the reagent is preferably not greater than 0.4.

Fig. 3 indicates Zisman plots which are generally used to estimate the surface energy of a solid body. In Fig. 3, a solid line and a dotted line indicate the silicone rubber according to the present invention and a generally available thermoplastic resin (polyvinylbutyral resin), respectively.

In general, the rubber density is required to be high and is preferably not less than 1.0. In applications where the rubber layer 10 includes no inorganic additive, the preferred density thereof ranges from 0.90 to 1.15 (the rubber density of 1.15 or greater renders the hardness to become high, and hence, such density cannot be employed). The higher the rubber density is, the less the thermally recorded colored material or a portion of a resin permeates or bites into the rubber layer 10. Accordingly, the use of the high-density rubber enables the colored material to be entirely transferred to the image receiving medium, and the continuous use thereof results in little changes with time, and therefore, such rubber can practically continuously be used. Although the apparent rubber density can be increased by the addition of an inorganic additive such as, for example, silica, an increase in cross-link density of a rubber material

brings about good results. The presence of the inorganic additive is a factor for increasing the adhesivity of the colored material to the rubber layer 10 during recording and increasing transfer residue. Accordingly, the amount of silica to be added to the rubber layer 10 is preferably so chosen as to be small enough to permit the rubber layer 10 to maintain a required physical strength, and, hence, preferably not higher than 20% by weight relative to the total weight of the rubber. It is most preferable to add no inorganic additive. Although silica can be added merely by dispersion, coupling the silicone rubber with activated silica, for example, silane-treated silica, brings about good results in increasing the rubber strength.

The coefficient of friction of the rubber layer 10 with respect to the standard paper is preferable not greater than 2. The use of the coefficient of friction of 2 or greater imparts a bonding property to the rubber layer 10 and lowers the ink releasability. The use of the coefficient of friction of 0.5 or smaller improves the ink releasability, but causes a reduction in ink recording capability or problems in driving the ink sheet or the image receiving medium by means of the intermediate recording medium. The preferred coefficient of friction with respect to the standard paper ranges from 1 to 1.5.

One or more of various kinds of silicone oils may be internally or externally added to the rubber layer 10 to improve the ink releasability of the rubber layer 10. When an oil takes the form of a liquid, it is preferable to extremely reduce the amount thereof to be added to the rubber layer 10. The preferred amount ranges from 0% to 5% by weight. The reason for this is that the continuous use of the intermediate recording medium renders the liquid silicone oil contained therein to be gradually transferred to the image receiving medium from the rubber layer 10. The reduction in the amount of the silicone oil inside the rubber layer 10 lowers the ink releasability of the rubber layer 10. Because the intermediate recording medium is occasionally used at temperatures below 80 °C, the inclusion of a solid release agent in the rubber layer 10 is considerably effective at temperatures below 100 °C. A carnauba-modified silicone oil having a melting point of 80 °C, a silicone oil modified with higher fatty acid ester, a silicone oil containing higher fatty acid, or the like is preferably used.

A solid material obtained by reacting two or more of various kinds of reactive oils each taking the form of a liquid at room temperatures, or a reactive oil cross-linkable to a silicone rubber is also effective. A material obtained by reacting an amino-modified oil and an epoxy-modified oil by equal weight is one typical example of the former. A carboxy- or amide-modified oil can also be used. A mercapto-modified oil is one typical example of

the latter. A main chain or a side chain of the rubber may be cross-linked to these reactive oils.

Because the inclusion of a thermoplastic or thermosetting resin with releasability in the silicone rubber increases the rubber hardness with the releasability maintained, the surface roughness of the rubber layer 10 does not become large even by the continuous use of the intermediate recording medium, and hence, such inclusion is particularly effective. Polyvinylbutyral, polystyrene, an AB resin, or the like is preferably used as a typical thermoplastic resin for this purpose, whereas an acrylic resin, an acrylurethane resin, or the like is preferably used as a typical thermosetting resin for this purpose. A siloxane resin having a dimethylsiloxane moiety at a portion of an acrylurethane silicone resin, or a fluororesin in which a portion of the siloxane resin is replaced by fluorine is also effective.

In order to externally add the second component of the above-described silicone rubber, the rubber layer 10 is made porous by extracting low-molecular components contained in the original silicone rubber using a solvent. By doing so, the second component can be externally added to the rubber layer 10, and subsequent heating stabilizes the second component inside the rubber layer 10. As occasion demands, the second component may be embedded in the rubber layer 10 under the conditions in which the second component is dissolved or dispersed in the solvent.

At least one kind of polyorganosiloxane (raw rubber) is used as a raw material of the silicone rubber according to the present invention. In preparing the silicone rubber, a reinforcing filler such as, for example, silica is initially added to the raw material, and a cross-linking agent, a polymerization initiator, a catalyst, and the like are added thereto and are subsequently subjected to heating for polycondensation or addition polymerization. A heat-curable silicone rubber or a malleable silicone rubber prepared by the so-called HTV (high-temperature vulcanizing) process can be used for this purpose. A room-temperature setting silicone rubber of the condensation or addition type prepared by the so-called RTV (room-temperature vulcanizing) process can also be used for this purpose. A heat setting silicone rubber prepared by the so-called LTV (low-temperature vulcanizing) process is also useful. Addition polymerization of a methylvinylsiloxane is particularly useful. Polycondensation or addition polymerization of a dimethylsiloxane, a methylphenylvinylsiloxane, a methylfluoroalkylsiloxane, or a mixture of these siloxanes is also used. A rubber in which some of methyl groups are replaced by groups containing fluorine or carbon fluoride is also useful. In this case, the ink releasability of the rubber becomes larger as a whole,

because the ink releasability of fluorine or carbon fluoride is large for a polar group.

One of the reasons why the ink releasability of the silicone rubber is high is that a solubility parameter (SP value) is small. The SP value of the silicone rubber is about 5, which is smaller than the SP value (6) of Teflon or is considerably smaller than the SP value (9-10) of ordinary resins. Because the use of Teflon causes insufficient releasability, it is important to maintain the SP value so as not to exceed 6 at the time the second component is added to the silicone rubber.

Parts or elements shown in Fig. 1 were prepared as follows.

Preparation of intermediate recording medium 1:

A PET film having a thickness of 50 microns was coated with a silicone rubber having a thickness of 0.4 mm by addition polymerization employing the following LTV process, and was wound around an aluminum drum accommodating a halogen lamp for heating the rubber up to 70 °C. In preparing the silicone rubber, a methylvinylsiloxane raw rubber having about 5000 siloxane units was used as a raw material, and 5 weight % of silane-treated silica was added and cross-linked thereto at 150 °C for one hour using a platinum catalyst.

Preparation of transfer medium (thermally fusible ink sheet):

Front and rear surfaces of a PET film having a thickness of 4 microns were coated with an ink layer having a thickness of 4 microns and a smooth heat-resistant layer having a thickness of 0.3 micron, respectively. The ratio of solid contents of the ink layer was as follows.

Wax (molecular weight: 1500): 30 weight %
Copolymer of ethylene and vinyl acetate (molecular weight: 100,000): 50 weight %
Long-chain fatty acid (molecular weight: 250): 5 weight %
Carbon black: 15 weight %

Image formation:

An inked image was transferred from the transfer medium to the intermediate recording medium by the thermal head for the recording of the inked image on the intermediate recording medium. The inked image was then transferred onto and fixed on a bond paper. The inked image was found to be a high-quality image. Even after the same image was recorded on five hundred thousand sheets of bond papers of an A4 size, no disorder was not caused in image quality. The conditions for image formation were as follows.

Thermal head: a resolving power of 12 dots/mm (A4 size)

Recording line speed: 2ms/line

Transfer/fixing pressure: 20 Kg•f/A4-width

Fig. 2 schematically depicts another thermal transfer printing apparatus employing the intermediate recording medium according to the present invention. As shown in Fig. 2, a transfer medium 2' is comprised of a base material 21 having a surface-treated layer 22 and is coated with a resin layer 6' of, for example, polyvinylbutyral and colored material layers 5' colored by the use of, for example, a sublimatable dye in this order in a direction of movement of the transfer medium 2'.

In the apparatus shown in Fig. 2, the entire resin layer 6' on the transfer medium 2' is initially thermally transferred on the silicone rubber layer 10 by the thermal head 3, and the dye contained in each of the colored layers 5' is subsequently thermally transferred onto the resin layer 6' by diffusion or vaporization and is recorded thereon. Thereafter, the dyed resin layer 6' is transferred onto and fixed on an image receiving medium 4. In Fig. 6, a reference numeral 6'' denotes the dyed resin layer fixed on the image receiving medium 4.

As is clear from the above, according to the present invention, because the ink releasability of the surface layer of the intermediate recording medium changes little with time, high-quality character images, multi-color images, or full-color images can be successively printed or recorded on a large number of, for example, tens of thousands of, standard papers or bond papers.

Although the present invention has been fully described by way of examples with reference to the accompanying drawings, it is to be noted here that various changes and modifications will be apparent to those skilled in the art. Therefore, unless such changes and modifications otherwise depart from the spirit and scope of the present invention, they should be construed as being included therein.

Claims

1. An intermediate recording medium (1) suited for thermal transfer printing wherein after a colored material (5, 5') held on a transfer medium (2, 2') or a resin layer (6'), held on the transfer medium (2, 2'), for holding thereon the colored material (5, 5') has been transferred onto the intermediate recording medium (1) by a recording head (3), the colored material (5, 5') or the resin layer (6') on the intermediate recording medium (1) is transferred onto and fixed on an image receiving medium (4), said intermediate recording medium (1) comprising:
 - a metallic drum (7); and

a silicone rubber layer (10) overlaid on said metallic drum (7) and having a thickness of 1 mm or smaller and a density of 0.90 to 1.15, a contact angle between said silicone rubber layer (10) and a reagent placed thereon having a cosine of 0.4 or smaller when said reagent has a surface tension of 45 dyn/cm or greater.

2. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains a dimethyl silicone oil in the range of 0 to 30% by weight.
3. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains 0% to 20% of silica by weight.
4. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) has a hardness of 20 to 60.
5. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains no inorganic additive and has a density of 0.90 to 1.15.
6. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains methyl groups, some of which include groups containing one of fluorine and carbon fluoride.
7. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) is formed by cross-linking reaction caused by addition polymerization of a methylvinyl silicone rubber.
8. The intermediate recording medium (1) according to claim 7, wherein said silicone rubber layer (10) is formed by coupling said silicone rubber with silane-treated silica.
9. The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains a solid release agent at a temperature below 100 °C.
10. The intermediate recording medium (1) according to claim 9, wherein said solid release agent contains at least one reactive silicone oil.
11. The intermediate recording medium (1) according to claim 10, wherein a main chain or a side chain of said silicone rubber is cross-linked to said reactive silicone oil, thereby pro-

viding said silicone rubber layer (10) with a colored material releasability by which the colored material (5, 5') is released from said silicone rubber layer (10).

- 12.** The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains thermoplastic or thermosetting polymeric components having a colored material releasability by which the colored material (5, 5') is released from said silicone rubber layer (10).

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- 13.** The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) has a solubility parameter (SP value) of 6 or smaller as a whole.

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- 14.** The intermediate recording medium (1) according to claim 1, wherein said silicone rubber layer (10) contains at least one of a dimethylsiloxane, a methylvinylsiloxane, a methylphenylvinylsiloxane, and a methylfluoroalkylsiloxane.

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- 15.** The intermediate recording medium (1) according to claim 1, wherein liquid components or low-molecular components contained in said silicone rubber layer (10) are removed by solvent-extraction.

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- 16.** The intermediate recording medium (1) according to claim 15, wherein said silicone rubber layer (10) contains fluid components and an additive which is solidified at temperatures below 100 °C.

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- 17.** The intermediate recording medium (1) according to claim 16, wherein said fluid components contain reactive silicone oils, a release agent which is solid at temperatures below 100 °C, and thermoplastic or thermosetting polymeric components dissolved or dispersed in a solvent.

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- 18.** The intermediate recording medium (1) according to claim 1, wherein said colored material (5, 5') is a thermally fusible ink.

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- 19.** The intermediate recording medium (1) according to claim 1, wherein said resin layer (6') for holding the colored material (5, 5') is dyed by diffusion or vaporization of a dye contained in the colored material (5, 5').

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Fig. 1

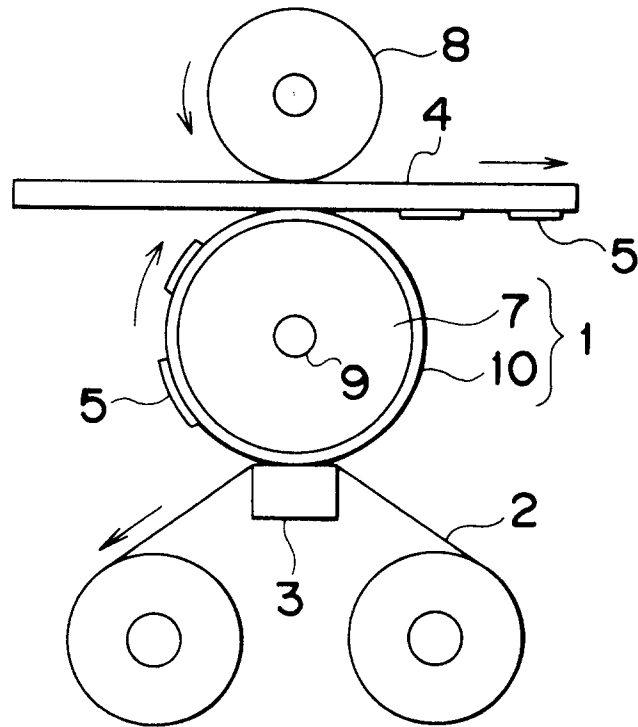


Fig. 2

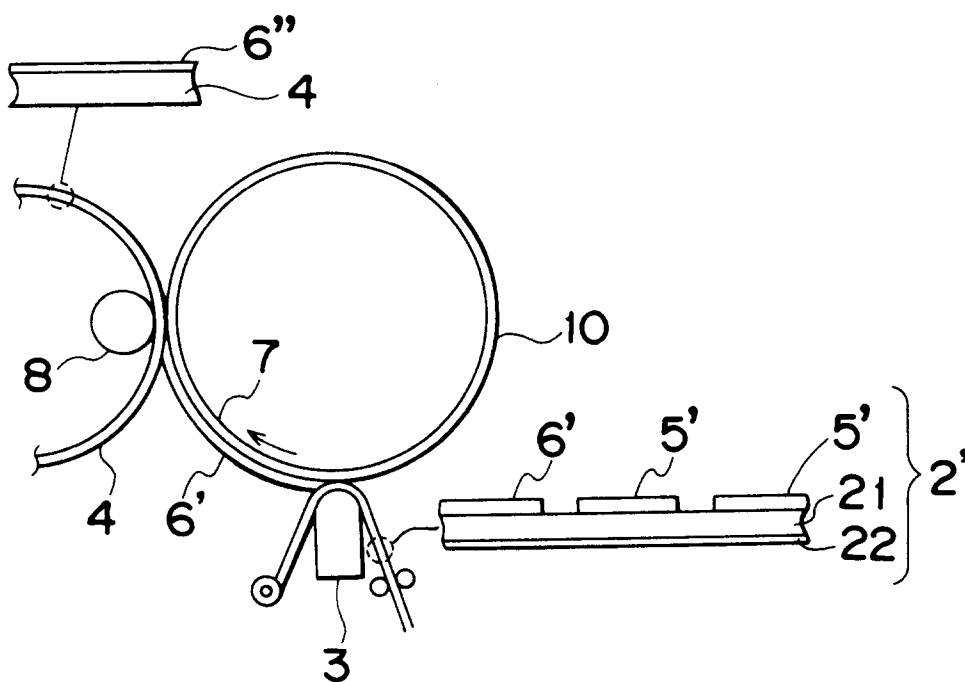
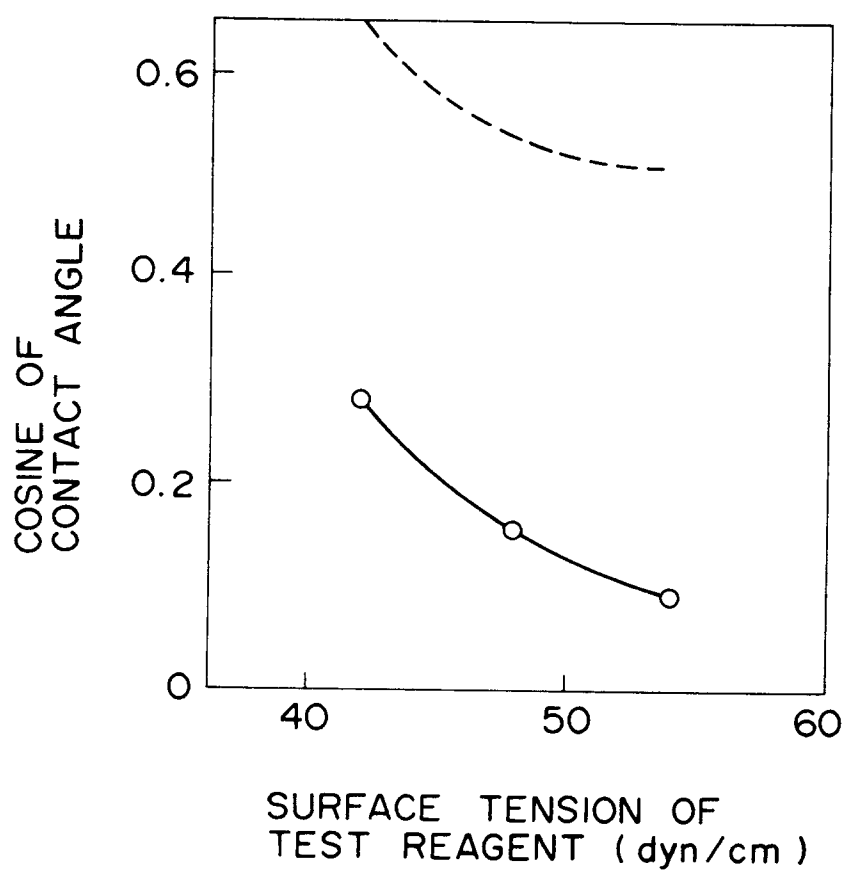


Fig. 3





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 5813

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)
X	EP-A-0 479 225 (MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED) * page 4, line 51 - page 5, line 1; claim 1; figure 1 * * page 6, line 44 - page 7, line 3 * ---	1-19	B41M5/38
X	EP-A-0 378 291 (MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED) * column 2, line 39 - column 3, line 22; claim 1; figure 1 * * column 5, line 20 - line 25 * ---	1-19	
A	FR-A-2 013 274 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 4, line 30 - page 8, line 9 * -----	1-19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 JUNE 1993	Examiner BACON A.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			