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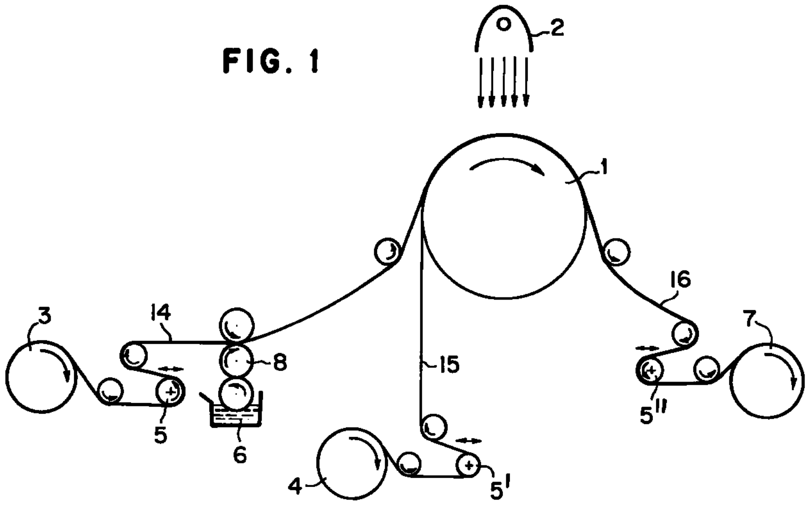
(54) High-sensitive stencil sheet and method for producing the same

(57) There are provided heat-sensitive stencil sheets which satisfactorily contacts with a thermal head and provide high quality images by enhancing the smoothness of the film surface of the heat-sensitive stencil sheets. Said heat-sensitive stencil sheets comprise a thermoplastic film and a porous support which are laminated to each other with an adhesive, characterized in that the glossiness indicating the smoothness of the film surface is 30% or higher and the adhering area ratio is 0.1-5%. The stencil sheet is obtained by carrying a porous support in close contact with the surface of a specular roll having a diameter of 0.1-1.5 m and a temperature of 15-90°C under a carrying tension of 0.1-5 kgf and simultaneously therewith carrying a thermoplastic film coated with 0.05-1.0 g/m^2 of a photocurable adhesive on one side and having a thickness of 2 μm or less under a given carrying tension thereby to allow the thermoplastic film to closely contact with the outer surface of the porous film with the adhesive therebetween and move the film and the support together on the specular roll, and curing the adhesive by irradiation with light above the specular roll.

FIG. 1



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Description

[0001] The present invention relates to a heat-sensitive stencil sheet and a method for producing the same. More particularly, it relates to a highly sensitive thermosensitive stencil sheet which is smooth in surface and provides excellent printing images, and a method for producing the same, which is high in productivity and stability of quality.

[0002] A printing system in which a stencil sheet is perforated by means of infrared rays, thermal heads and the like and is used as a master for printing is known as stencil printing and widely spread as a convenient printing system. The perforation method using a thermal head is called digital perforation and is presently a major perforation system because the background part is hardly stained, letters or figures can be digitized and it is easy to operate. Furthermore, with recent increase in demand for high-quality printing of high resolution adapted for from small letters to halftone of photographs, heating elements of the thermal head employed in the perforation apparatus has been made highly minute and precise. Moreover, in order to prolong the life of the thermal head having the minute and precise elements, a perforation system with low energy is demanded.

[0003] Heat-sensitive stencil sheets are also being investigated in an attempt to enhance sensitivity for attaining perforation with low energy and furthermore conform to the thermal head having the highly minute and precise elements. As a method for enhancing sensitivity of a heat-sensitive stencil sheet comprising a laminate of a thermoplastic film and a porous support, it can be considered to use a high sensitive thermoplastic film thin in thickness (e.g., less than 2μm), low in melting point and high in thermal shrinkage. A heat-sensitive stencil sheet having such a high sensitivity thermoplastic film can be easily perforated using a high resolution thermal head or a low energy thermal head. However, when such a highly sensitive thermoplastic film is laminated on the surface of a porous support, unevenness occurs on the film surface in conformity with the rugged configuration of the support and the film surface does not closely contact with the thermal head at the time of perforation. As a result, the portions which are not perforated owing to the insufficient contact appear as white spots in the printed images to cause so-called "voids".

[0004] According to the conventional laminating method, as shown in FIG. 3, a thermoplastic film 14 drawn from film roll 3 is carried under application of a constant tension by tension controlling roll 5 while a porous support 15 drawn from porous support roll 4 is similarly carried under application of a constant tension by tension controlling roll 5'. After coating one side of the thermoplastic film 14 with adhesive 6 by coating rolls 8, the thermoplastic film 14 and the porous support 15 are pressure bonded by nip rolls 11, and then wound up by stencil sheet wind-up roll 7 under application of tension by tension control rolls 5", during which the adhesive 6 is hardened by heat-drying means or light-irradiation means 2, thereby obtaining a heat-sensitive stencil sheet. Therefore, there is a problem that at the time of pressure bonding by the nip rolls 11, the bonding area increases and simultaneously the ruggedness of the surface of the porous support are transferred to the thermoplastic film to damage the smoothness of the film. Furthermore, there is another problem that since after being pressure bonded, the film 14 and the support 15 are passed through a furnace provided with a heating means or light-irradiation means 2 in a free state under no constraint, viscosity of the adhesive decreases due to the heat in the furnace to cause peeling at bonding spots, namely, so-called delamination phenomenon.

[0005] Various methods have been proposed to solve these problems. For example, in order to increase surface smoothness of heat-sensitive stencil sheets, JP-B-3-52354 has proposed a method according to which as shown in FIG. 4 a thermoplastic film 14 drawn from a film roll 3 is coated with an adhesive 6 by a coating roll 8, then the film 14 is carried in close contact with a specular roll 1 with the side of the film 14 coated with the adhesive 6 being faced outwardly while the porous support 15 drawn from a support roll 4 is allowed to closely contact with the film 14 on the specular roll 1, simultaneously therewith the adhesive 6 is dried by a hot air drier 12 to laminate the film and the support, and then the laminate is cooled by a cooling roll 13 and wound up by a stencil sheet wind-up roll 7.

[0006] The above method can provide heat-sensitive stencil sheets of high smoothness, but suffers from the following various problems because a solvent type adhesive, especially organic solvent soluble type adhesive is used as the adhesive 6 and is cured by drying with heat. That is, if the coating amount is larger than 1.0 g/m^2, puddles of the adhesive are sometimes formed on the surface of the film and failure of perforation occurs at the portions of the puddles. Moreover, the laminate must be heated to a high temperature of higher than 90°C, in some case, higher than 120°C to dry and cure the adhesive, and when the film 14 is a high sensitive thermoplastic film, this is readily annealed to cause deterioration of smoothness after storing the heat-sensitive stencil sheet in the form of a roll for a long period of time, and, in the worst case, the smoothness is seriously damaged due to shrink of the film just after lamination. In addition, when an organic solvent type adhesive is used, volatilization of the organic solvent pollutes the working atmosphere or the organic solvent of the adhesive volatilizes during suspension of production lines and this often causes change in viscosity. Thus, there are problems in working atmosphere, production atmosphere and productivity.

[0007] Moreover, in order to increase the surface smoothness of heat-sensitive stencil sheets, JP-A-7-61159 has proposed a method according to which as shown in FIG. 5, one side of a porous support 15 drawn from a support roll 4 is coated with an adhesive 6 by a coating roll 8, the adhesive-coated side of the support 15 is directly pressure bonded to the surface of a thermoplastic film on roll 3 to laminate them, and the laminate is wound up by stencil sheet wind-up roll 7, during which the adhesive 6 is dried and cured by a hot-air drier 12. However, like the method of FIG. 3, in this method, the laminated film and support are carried in a free state under no constraining force at the drying and curing step of the adhesive after pressure bonding, and, hence, the delamination phenomenon is apt to occur. Furthermore, since the pressure bonding between the porous support and the thermoplastic film is weak and, besides, bonding distance and time are short, they are bonded at a few points to decrease the bonding area ratio. As a result, the thermoplastic film and the porous support are readily separated, and especially when a large number of copies are printed, the thermoplastic film and the porous support are readily separated due to the extension of the porous support to result in a problem in printing endurance.

[0008] On the other hand, JP-A-10-193826 discloses a heat-sensitive stencil sheet having a glossiness of film surface of 30% or more and excellent in perforation property, namely, image formation property. However, the stencil sheet is produced by hot bonding a porous support and a thermoplastic film and then co-stretching them, and is not produced by laminating the thermoplastic film and the porous support using adhesives.

[0009] As explained above, it is needed to use thermoplastic films of the higher sensitivity in heat-sensitive stencil sheets for speeding up of perforation and for use of highly minute thermal heads. On the other hand, according to the conventional methods for the production of stencil sheets, smoothness of the film is deteriorated due to the rugged surface of the porous support, voids are formed due to failure of perforation to deteriorate image properties, and delamination phenomenon occurs when coating amount of the adhesive is reduced. Thus, it has been found that the conventional methods are not suitable for the production of stencil sheets using thermoplastic films of high sensitivity.

[0010] The object of the present invention is to provide a heat-sensitive stencil sheet free from these problems which is high in glossiness of the surface of film, satisfactorily contacts with a thermal head, can give high image quality, and is excellent in stability of quality and productivity, and a method for producing said heat-sensitive stencil sheet.

[0011] As a result of intensive research conducted by the inventors in an attempt to attain the above object, they have succeeded in providing a heat-sensitive stencil sheet comprising a thermoplastic film and a porous support which are laminated to each other with an adhesive wherein glossiness indicating the smoothness of the film surface is 30% or higher and adhering area ratio is 0.1-5%, and it has been found that the above object can be attained by this heat-sensitive stencil sheet. Thus, the present invention has been accomplished.

[0012] The heat-sensitive stencil sheet of the present invention can be produced, for example, by a method which comprises carrying a porous support in close contact with the surface of a specular roll under a given carrying tension while a thermoplastic film coated with a given amount of a photo-curable adhesive on one side is carried under a given carrying tension, allowing the thermoplastic film to closely contact with the outer surface of the porous support on the specular roll with the adhesive being present between the thermoplastic film and the porous support whereby the thermoplastic film and the porous support are moved together, and curing the adhesive above the specular roll by irradiation with light.

FIG. 1 is a diagrammatic illustration which shows an example of the method for producing the heat-sensitive stencil sheet of the present invention.

FIG. 2 is a diagrammatic illustration which shows another example of the method for producing the heat-sensitive stencil sheet of the present invention.

FIG. 3 is a diagrammatic illustration which shows a conventional method for producing the heat-sensitive stencil sheet.

FIG. 4 is a diagrammatic illustration which shows a method for producing a heat-sensitive stencil sheet disclosed in JP-B-3-52354.

FIG. 5 is a diagrammatic illustration which shows a method for producing a heat-sensitive stencil sheet disclosed in JP-A-7-61159.

[0013] According to the method of the present invention mentioned above, a thermoplastic film coated on one side with a given amount of an adhesive comprising a photo-curable resin is allowed to closely contact with a porous support previously held on a specular roll in close contact with the surface of the roll and these are carried together, during which these are irradiated with light. Therefore, curing of the adhesive can be completed simultaneously with lamination of the thermoplastic film and the porous support while the smooth surface of the thermoplastic film and the porous support are held on the specular roll. Thus, it becomes possible to produce a heat-sensitive stencil sheet high in smoothness, and a heat-sensitive stencil sheet having an adhering area ratio of 0.1-5% and a glossiness of 30% or higher can be produced. If the adhering area ratio is less than 0.1%, adhesion between the film and the support is insufficient, and the thermoplastic film peels off when a large number of prints are printed to cause so-called delamination phenomenon, resulting in a problem in printing endurance. If the adhering area ratio exceeds 5%, the adhesive is retained between the fibers of the porous support to cause formation of voids in the prints, and, furthermore, unevenness of the surface of the support is often transferred to the thermoplastic film to lower the glossiness. In the method of the present invention, it is generally preferred that the coating amount of the adhesive is 0.05-1.0 g/m^2 and the carrying tension for the thermoplastic film and the porous support is controlled to 0.1-5 kgf, and under these conditions, the heat-sensitive stencil sheet of the present invention can be produced most satisfactorily.

[0014] The method of the present invention will be explained in detail referring to FIG. 1. A thermoplastic film 14 drawn from film roll 3 is carried under a given tension through tension control roll 5 and fed to a coating roll 8 by which a given amount of adhesive 6 is coated on one side of the film. A porous support 15 drawn from support roll 4 is similarly carried under a given tension through tension control roll 5' and is moved so as to closely contact with the outer peripheral surface of a specular roll 1. The thermoplastic film 14 is superposed on the porous support 15 positioned on the specular roll 1 so that the side of the thermoplastic film 14 coated with the adhesive 6 closely contacts with the outer surface of the porous support 15, namely, the side opposite to the side contacting with the specular roll 1, and the thermoplastic film 14 and the porous support 15 are moved at the same peripheral speed under being press-bonded only by a weak force given by the tension of the porous support and the film. In this case, by the irradiation with light by a light irradiation device 2 just above the specular roll 1, the adhesive is cured while the thermoplastic film 14 and the porous support 15 are moved in the state of their smoothness being maintained under the above-mentioned tension on the surface of the specular roll 1. Thus, the adhering area ratio is controlled and a heat-sensitive stencil sheet excellent in smoothness can be produced at high speed. The heat-sensitive stencil sheet 16 comprising the laminate formed in this way is wound up on the stencil sheet wind-up roll 7 through the tension control roll 5'' for the adjustment of the winding tension.

[0015] FIG. 2 shows a modified example of the method of FIG. 1, where the elements indicated by the same reference numerals as in FIG. 1 are the same elements as in FIG. 1. The method shown by FIG. 2 differs from the method of FIG. 1 in that in addition to the specular roll 1, there is provided another specular roll 1' disposed adjacent to the specular roll 1 on the downstream side in the machine direction. In the method of FIG. 2, the heat-sensitive stencil sheet formed by lamination on the specular roll 1 as in FIG. 1 is further fed to the specular roll 1' revolving in the opposite direction to the specular roll 1 where the side of the thermoplastic film 14 of the stencil sheet is allowed to closely contact with the specular roll 1' and simultaneously the side of the porous support 15 of the stencil sheet is irradiated with light by a light irradiation device 2' to accelerate curing of the adhesive 6. In this way, in the method of FIG. 2, the adhesive is cured by charging energy from both sides of the stencil sheet, and, hence, production speed can easily be increased. Similarly, additional specular rolls can be provided to increase the production speed.

[0016] The specular rolls used in the present invention are preferably those which have a diameter of 0.1-1.5 m and have surfaces subjected to specular finishing by conventional methods such as plating with chromium or nickel. The diameter is more preferably 0.1-1.0 m. If the diameter is less than 0.1 m, since a sufficient curing time of the adhesive cannot be taken, not only the stencil sheet can hardly be produced at a practically acceptable production speed, but also the curvature of the specular roll is transferred to the heat-sensitive stencil sheet and the resulting stencil sheets have a large curling. On the other hand, if the diameter of the specular roll exceeds 1.5 m, there is no problem in productivity, but the equipment becomes large or the production cost increases, and this is not practical. Moreover, at the time of production of the stencil sheets, the specular roll is preferably kept at a constant temperature in the range of 15-90°C, more preferably kept at 30-60°C. If the temperature of the specular roll is lower than 15°C, curing speed of the adhesive lowers to make it difficult to ensure a practically acceptable production speed. On the other hand, if the temperature of the specular roll is higher than 90°C, annealing phenomenon occurs in the thermoplastic film to lower heat sensitivity, and, in the worst case, there occurs a problem such as shrinkage of the thermoplastic film. For keeping the specular roll at a constant temperature, a pipe through which a temperature regulation medium such as water or oil is passed is provided inside the specular roll, a cold air is blown against a part of the specular roll, or another cooling roll is allowed to contact with the specular roll.

[0017] The thermoplastic films in the present invention may be those which are perforated and shrink by the heating at the time of making masters, and examples thereof are polyolefin films such as polyethylene film and polypropylene film, polystyrene films, polyester films, polyvinyl chloride films, polyvinylidene chloride films, and polyvinylidene fluoride films. Of these films, polyester films are preferred because they are excellent in strength when made into thin films. Furthermore, for carrying out the low-energy master making which recently becomes predominant in the field of heat sensitive stencil printing, preferred are high-sensitive thermoplastic resin films of 2 μm or less in thickness and 1% or more in heat area shrinkage at 80°C.

[0018] The porous supports in the present invention may be any of those which can support the thermoplastic film and have a structure capable of passing an ink therethrough in printing. Examples thereof are sheets made by wet or dry method from one or a mixture of natural fibers such as wood pulp, hemp, mitsumata (Edgeworthia papyrifera) and paper mulbery, and chemical fibers such as rayon, vinylon, nylon, polyester, polyphenylene sulfide and acrylonitrile. The supports are not particularly limited in basis weight and thickness, but the basis weight is suitably about 5-20 g/m^2 from the points of consumption of ink, strength and handleability.

[0019] As the adhesives in the present invention, photo-curable adhesives are used for the following reasons: the high-speed production is possible; the curing temperature is low to give no heat damage to the thermoplastic films; and they are solventless and one-pack type adhesives and small in change of viscosity. The term "photo-curable adhesives" in the present invention is interpreted in a broad sense and includes those which are cured by infrared ray, visible ray, ultraviolet ray, electron beam, and the like. Moreover, if necessary, these adhesives may contain various additives such as antistatic agent, lubricant and leveling agent.

[0020] The photo-curable adhesives mainly comprise a monomer, an oligomer and a photopolymerization initiator, and as for the ratio of the monomer and the oligomer, the monomer is preferably 20-100 w/w%, more preferably 20-95 w/w%, further preferably 50-95 w/w%, and the oligomer is preferably 0-80 w/w%, more preferably 5-80 w/w%, further preferably 5-50 w/w%. The adhesives may further contain high polymers and additives. If the ratio of the oligomer exceeds 50 wt%, viscosity of the adhesives becomes too high and coating operation becomes difficult. If it is lower than 20 wt%, curing speed becomes lower or adhesive strength decreases.

[0021] The monomers include, for example, monofunctional acrylic monomers having one (meth)acryloyl group in the molecule and polyfunctional acrylic monomers having two or more (meth)acryloyl groups in the molecule. The monofunctional acrylic monomers include, for example, acrylic monomers having cyclic structure such as aliphatic ring, aromatic ring or heterocyclic ring and aliphatic acrylates having a hydroxyl group. As the acrylic monomers having cyclic structure such as aliphatic ring, aromatic ring or heterocyclic ring, mention may be made of, for example, tricyclodecane (meth)acrylate, dicyclopentenyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, morpholine acrylate, and phenylglycidyl (meth)acrylate. Furthermore, alkylene oxide modified products of these compounds can also be used. Especially preferred are modified products in which alkylene oxide has 2-3 carbon atoms, and examples are dicyclopentenyloxyethyl (meth)acrylate and phenyloxyethyl (meth)acrylate. As the aliphatic acrylates having a hydroxyl group, preferred are acrylates in which the hydroxyl group bonds to an aliphatic group of 2-9 carbon atoms, more preferred are acrylate compounds in which the hydroxyl group bonds to an aliphatic group of 2-4 carbon atoms. The aliphatic acrylates may contain a substituent such as phenoxy group. As the aliphatic acrylates having a hydroxyl group, mention may be made of, for example, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate.

[0022] Among these monofunctional acrylic monomers, especially preferred for maintaining viscosity, resistance to moist heat, and adhesive force are phenyloxyethyl (meth)acrylate, tricyclodecane (meth)acrylate, isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, morpholine acrylate, 2-hydroxyethyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate. The polyfunctional acrylic monomers are classified into bifunctional acrylic monomers and trifunctional or higher functional acrylic monomers. Examples of the bifunctional acrylic monomers are acrylate compounds of aliphatic diols of 4-9 carbon atoms, alkylene oxide type acrylic monomers and acrylic monomers having a cyclic structure.

[0023] The acrylate compounds of aliphatic diols of 4-9 carbon atoms include, for examples, neopentyl glycol di(meth)acrylate and 1,6-hexanediol (meth)acrylate. These acrylate compounds of aliphatic diols may be modified with an aliphatic ester or an alkylene oxide. Examples of the aliphatic ester-modified acrylate compounds are neopentyl glycol hydroxypivalic acid di(meth)acrylate and caprolactone-modified neopentyl glycol hydroxypivalic acid di(meth)acrylate. Examples of the alkylene oxide-modified acrylate compounds are diethylene oxide-modified neopentyl glycol di(meth)acrylate, dipropylene oxide-modified neopentyl glycol di(meth)acrylate, diethylene oxide-modified 1,6-hexanediol (meth)acrylate, and dipropylene oxide-modified 1,6-hexanediol (meth)acrylate.

[0024] The alkylene oxide type acrylic monomers include, for example, neopentyl glycol-modified trimethylolpropane di(meth)acrylate, polyethylene glycol di(meth)acrylate and polypropylene glycol di(meth)acrylate. The acrylic monomers having cyclic structures include, for example, tricyclodecanedimethylol di(meth)acrylate and dicyclopentanyl di(meth)acrylate.

[0025] The trifunctional or higher functional acrylic monomers include, for example, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, C_{2-5} aliphatic hydrocarbon-modified dipentaerythritol penta(meth)acrylate, C_{2-5} aliphatic hydrocarbon-modified dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol hexa(meth)acrylate, dipentaerythritol tetra(meth)acrylate, tris[(meth)acryloxyethyl] isocyanurate, caprolactone-modified tris[(meth)acryloxyethyl] isocyanurate, and ditrimethylolpropane tetra(meth)acrylate.

[0026] Among these polyfunctional acrylic monomers, especially preferred for maintaining viscosity, resistance to moist heat, and adhesive force are bifunctional acrylic monomers, for example, acrylate compounds of aliphatic dials of 4-9 carbon atoms such as neopentyl glycol di(meth)acrylate and 1,6-hexanediol (meth)acrylate, and aliphatic ester-modified aliphatic diol acrylates such as neopentyl glycol hydroxypivalic acid di(meth)acrylate and caprolactone-modified neopentyl glycol hydroxypivalic acid di(meth)acrylate, and trifunctional or higher functional acrylic monomers such as dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, tris[(meth)acryloxyethyl] isocyanurate and caprolactone-modified tris[(meth)acryloxyethyl] isocyanurate.

[0027] Amount of these monomers is preferably about 5-90% by weight based on the total weight of the adhesive composition. These monomers may be used each alone or in admixture of two or more at an optional ratio, but from the point of viscosity, the monofunctional acrylic monomers or bifunctional acrylic monomers are preferred and the trifunctional or higher functional acrylic monomers may be used as required. As mentioned above, if the adhesives are required to have the higher adhesive strength or endurance (inhibition of deterioration), oligomers can be used in combination. Oligomers usable in the present invention preferably are soluble in the monomers and have two or more (meth)acryloyl groups in the molecule. Examples of such oligomers are epoxy (meth)acrylate, polyester (meth)acrylate and urethane acrylate.

[0028] The epoxy (meth)acrylate is obtained by a reaction of an epoxy resin with (meth)acrylic acid. Examples of the epoxy resin are bisphenol type epoxy resins such as bisphenol A epoxy resin and bisphenol F epoxy resin, and novolak type epoxy resins. As examples of the bisphenol A epoxy resin, mention may be made of EPIKOTE [trademark (same in the following)] 828, EPIKOTE 1001 and EPIKOTE 1004 manufactured by Yuka Shell Epoxy Co., Ltd., and as examples of the bisphenol F epoxy resins, mention may be made of EPIKOTE 4001P, EPIKOTE 4002P and EPIKOTE 4003P manufactured by Yuka Shell Epoxy Co., Ltd. Examples of the novolak type epoxy resins are EPIKOTE 152 and EPIKOTE 154 manufactured by Yuka Shell Epoxy Co., Ltd.

[0029] The polyester (meth)acrylate is obtained by the reaction of a polyester polyol with (meth)acrylic acid. The polyester polyol is obtained by the reaction of a polyhydric alcohol with a polybasic acid. Examples of the polyhydric alcohol are neopentyl glycol, ethylene glycol, propylene glycol, 1,6-hexanediol, trimethylolpropane, pentaerythritol, tricyclodecane dimethylol and bis-[hydroxymethyl]-cyclohexane. Examples of the polybasic acid are succinic acid, phthalic acid, hexahydrophthalic anhydride, terephthalic acid, adipic acid, azelaic acid and tetrahydrophthalic anhydride.

[0030] As examples of the urethane (meth)acrylate, mention may be made of those which are obtained by the reaction of the three of a polyol, an organic polyisocyanate and a hydroxy(meth)acrylate compound and those which are obtained by the reaction of the two of the organic polyisocyanate and the hydroxy(meth)acrylate compound without using the polyol. Examples of the polyol are polyether polyols such as polypropylene glycol and polytetramethylene glycol, polyester polyols obtained by the reaction of the above polyhydric alcohol and the above polybasic acid, caprolactone polyols obtained by the reaction of the above polyhydric alcohol, the above polybasic acid and ε-caprolactone, and polycarbonate polyols (e.g., polycarbonate polyols obtained by the reaction of 1,6-hexanediol with diphenyl carbonate). Examples of the organic polyisocyanate are isophorone diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate, xylene diisocyanate, diphenylmethane-4,4'-diisocyanate and dicyclopentanyl diisocyanate. Those which are obtained by the reaction of the two or the three can be used each alone or in combination of two or more. Of these oligomers, especially preferred for maintaining viscosity, resistance to moist heat and adhesive force are epoxy (meth)acrylates and urethane (meth)acrylates. These oligomers can be used each alone or in admixture of two or more at an optional ratio.

[0031] As examples of the photopolymerization initiators, mention may be made of the compounds such as 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, Michler's ketone, 2-chlorothioxanthone, 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, isopropylthioxanthone, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1. These photopolymerization initiators may be used each alone or in admixture of two or more. Moreover, these may be mixed with amine photopolymerization initiation aids such as 4-diethylaminoethyl benzoate, 2-dimethylaminoethyl benzoate, dimethylaminoacetophenone, p-dimethylaminobenzoate, and isoamyl p-dimethylaminobenzoate. Amount of the photopolymerization initiation aids is preferably about 0-15% by weight, more preferably about 0-10% by weight based on the total weight of the adhesive composition.

[0032] As a curing device which is disposed above the specular roll and cures the photo-curable adhesive, a known light irradiation device can be used as it is, and examples of the curing device are pressure or high pressure mercury lamps, metal halide lamps, xenon lamps, electrodeless discharge lamps or carbon arc lamps, and various electron beam accelerators such as of Cockcroft-Walton type, Van de Graaff type, resonance transformation type, insulation core transformer type, linear type, electro curtain type, dynamitron type, and high frequency type in the case of curing with electron beams.

[0033] The heat-sensitive stencil sheet of the present invention, namely, the heat-sensitive stencil sheet which has an adhering area ratio of 0.1-5% between the thermoplastic film and the porous support and a glossiness of 30% or higher as an indication of smoothness of the film surface can be produced by allowing the thermoplastic film and the porous support to closely contact with each other on a smooth specular roll and simultaneously curing the adhesive, and, besides, by suitably selecting the coating amount of the adhesive, press bonding force of the thermoplastic film and the porous support (namely, diameter of the specular roll and tension of the thermoplastic film and the porous support), carrying speed of the thermoplastic film and the porous support (which is equal to the curing speed of the adhesive), temperature of the specular roll, etc. depending on the kind of the film or the support used.

[0034] In order to adjust the glossiness of the film surface of the heat-sensitive stencil sheet to 30% or higher, it is desirable to control the coating amount of the adhesive within the range of 0.05-1.0 g/m^2. If the coating amount is less than 0.05 g/m^2, the adhesive can not sufficiently be present at adhering points of the fibers of the porous support and the thermoplastic film, resulting in delamination phenomenon. If the coating amount is more than 1.0 g/m^2, the adhering area ratio increases to cause deterioration of the glossiness or to cause puddles of the adhesive on the film surface present between the fibers of the porous support. As a result, failure of perforation of the thermoplastic film is brought about in making masters, and a phenomenon of void formation occurs in printing.

[0035] Furthermore, in order to produce stencil sheets free from delamination and wrinkling and less in curling with maintaining the adhering area ratio within a proper range, it is desirable to adjust the carrying tension of the thermoplastic film and the porous support to a range of 0.1-5 kgf. If the tension is less than 0.1 kgf, the press bonding force between the thermoplastic film and the porous support is insufficient, and the number of the adhering points is very small or there are present portions which are not adhered. If the tension is more than 5 kgf, the adhering area ratio is apt to exceed 5%, and a large proportion of the unevenness of fibers of the porous support is transferred to the thermoplastic film to cause decrease of glossiness, failure of perforation and great curling.

[0036] The photo-curable adhesives of the present invention can be coated by the means such as multi-roll coating method, blade coating method, gravure coating method, knife coating method, reverse-roll coating method, spray coating method, offset gravure coating method and kiss-roll coating method.

[0037] The heat-sensitive stencil sheet of the present invention has the excellent perforation characteristics as mentioned above. However, when the stencil perforations are formed by heating the thermoplastic resin film by the means such as thermal head and the like, there is the possibility of the thermal head sticking to the thermoplastic resin film of the stencil sheet to damage the stencil sheet, and when the stencil perforations are formed by superposing a positive original film on the film side of the stencil sheet and exposing them to light, there is the possibility of the positive original film being fusion bonded to the film of the stencil sheet. For the solution of these problems, it is preferred to form a fusion bonding inhibition layer on the thermoplastic resin film layer of the stencil sheet. For the formation of such fusion bonding inhibition layer, there may be used, for example, fluorocarbon polymers such as polytetrafluoroethylene, polychlorotrifluoroethylene, tetrafluoroethylenehexafluoroethylene copolymer and polyvinylidene fluoride, silicone resins, epoxy resins, melamine resins, phenolic resins, polyimide resins, polyvinyl acetal resins, polyvinyl butyral resins, polyoxyethylene terephthalate and polyethylene oxide resins. Furthermore, for the purpose of improving slipperiness of the fusion bonding inhibition layer, there may be added surface active agents, for example, fatty acid metallic salts such as lithium, potassium, sodium, calcium, barium and aluminum salts of stearic acid, palmitic acid, lauric acid or oleic acid, phosphate ester type surface active agents, polyoxyethylene type surface active agents, mono- or di-alkyl phosphate esters, and tri(polyoxyethylenealkyl ether) phosphate esters. Moreover, there may also be used fusion bonding inhibitors comprising ultraviolet ray-curable silicone resins as disclosed in JP-B-4-73395. In this case, curing of the photo-curable adhesive and curing of the fusion bonding inhibitor can be simultaneously performed on the specular roll, and this is preferred. If the coating amount of the fusion bonding inhibitor is too large, heat sensitivity lowers and formation of perforation becomes insufficient. Therefore, the coating amount is preferably such as to form a thin layer, and, desirably, about 0.001-0.5 g/m^2.

[0038] The present invention will be explained in more detail by the following examples. The evaluation tests in the examples were conducted by the following methods.

(1) Glossiness:

[0039] This was measured in accordance with JIS Z 8741 (test method for specular glossiness) (method 5). That is, a sheet of white neutral paper (RISO PAPER/USUKUCHI (trade name) manufactured by RISO KAGAKU CORPORATION) was put on a horizontal and flat table, and thereon was put a heat-sensitive stencil sheet with the film side facing upward. The glossiness was measured by a gloss meter (GM-268 manufactured by Minolta Co., Ltd.) with an incident angle of 20° . The measurement was conducted on five positions in widthwise direction of the stencil sheet of A3 in size, and the average value was obtained with counting fractions of .5 and over as a unit and cutting away the rest.

(2) Adhering area ratio:

[0040] The film surface of the heat-sensitive stencil sheet was observed by a light microscope of one hundred magnifications, and the area ratio of the adhering portions was calculated by picture processing.

(3) Rate of failure in perforation:

[0041] A master of whole solid patterns was made using stencil printing machine mounted with a thermal head of 600 dpi (RISOGRAPH (registered trademark) GR377 manufactured by RISO KAGAKU CORPORATION) under normal perforation conditions. The film surface of the heat-sensitive stencil sheet was photographed by a stereoscopic microscope of fifty magnifications. The rate of failure in perforation was obtained as a proportion of the number of unperforated dots in 2400 dots in total which were heated by the thermal head.

(4) Printing endurance:

[0042] Printing was carried out at a printing speed of 150 prints/min by a stencil printing machine (RISOGRAPH (registered trademark) GR377 manufactured by RISO KAGAKU CORPORATION). When none of wrinkling, peeling and breakage of film occurred even after printing of 3000 prints, this is indicated by "○", and when either one of wrinkling, peeling or breakage of film occurred before printing of 300 prints, this is indicated by "X".

(5) Quality of image:

[0043] Printing was carried out at a printing speed of 150 prints/min by a stencil printing machine (RISOGRAPH (registered trademark) GR377 manufactured by RISO KAGAKU CORPORATION). Degree of formation of voids in the 100th print was visually observed and the results were evaluated by the following criteria.

○: Good.
X: Bad.
△: Between good and bad.

(6) Curling (flatness of stencil sheet):

[0044] A heat-sensitive stencil sheet was cut in the form of a square of 100 × 100 mm so that one of the diagonal lines of the square parallels the carrying direction in lamination, and the square sheet was left to stand for 5 minutes on a horizontal stand. When the height of one side of the sheet which curled up to maximum was 10 mm or lower, this is indicated by "○", and when the height was higher than 10 mm, this is indicated by "X".

(7) Delamination phenomenon:

[0045] The heat-sensitive stencil sheet after lamination was visually observed. When no peeling was observed between the porous support and the thermoplastic film, this is indicated by "○", and when even a slight peeling was observed, this is indicated by "X".

(8) Wrinkling:

[0046] The heat-sensitive stencil sheet after lamination was visually observed. When no crepe-like wrinkles were observed, this is indicated by "○", and when even slight crepe-like wrinkles were observed, this is indicated by "X".

Examples 1-7 and Comparative Examples 1-6

[0047] A high-sensitive polyester film having a heat area shrinkage of 2% at 80°C, and a width of 240 mm and a thickness of 1.8 µm was used as a thermoplastic film. A porous support used had a width of 240 mm and a basis weight of 12 g/m^2 and comprised mixed fibers containing 30 wt% of polyester fibers and 70 wt% of Japanese paper fibers. Adhesives as shown in Table 1 were used. In the case of using the apparatuses of FIG. 1 and FIG. 2, a hot air drier of 120°C or an ultraviolet irradiation device comprising a metal halide lamp of 80 W/cm was used as a drying and curing means for the adhesive. The ultraviolet irradiation device was provided with a light reflector disposed around the metal halide lamp so as to surround the specular roll. The drying and curing means was positioned at a distance of 10 cm from the specular roll. In the case of using the apparatus of FIG. 3, the similar ultraviolet irradiation device was positioned at a distance of 10 cm from the laminate stencil sheet. Furthermore, 0.05 g/m^2 of an silicone oil having a viscosity of 100 cst at 25°C was coated as a fusion bonding inhibitor by after-treatment.

[0048] Heat-sensitive stencil sheets were prepared under the conditions as shown in Table 2. The results are shown in Table 3.

Table 1

Component	Adhesive I	Adhesive II
Kind	Ultraviolet ray curing type	Solvent type
A	-	20

Table 1 (continued)

Component	Adhesive I	Adhesive II
Kind	Ultraviolet ray curing type	Solvent type
B	-	80
C	40	-
D	60	-
E	2	-
F	2	-

[0049] In Table 1,

A: Byron 500 (a polyester resin manufactured by Toyobo Co., Ltd.)
B: Ethyl acetate
C: Urethane acrylate
D: 2-Hydroxy-3-phenoxypropyl acrylate
E: 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1
F: 4-Diethylaminoethyl benzoate

Table 2

	Example							Comparative Example					
	1	2	3	4	5	6	7	1	2	3	4	5	6
Method of production	Fig. 1	Fig. 1	Fig. 1	Fig. 1	Fig. 1	Fig. 1	Fig. 2	Fig. 1	Fig. 1	Fig. 1	Fig. 3	Fig. 1	Fig. 1
Adhesives	I	I	I	I	I	I	I	II	I	I	I	I	I
Coating amount of adhesive(g/m^2)	0.3	0.8	0.5	0.5	0.5	0.5	0.5	0.5	2.0	0.5	0.5	0.5	0.5
Carrying tension(kgf)	1.0	1.0	0.5	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.05	7
Dry and curing means	UV	UV	UV	UV	UV	UV	UV	Hot air	UV	UV	UV	UV	UV
Line speed(m/min)	40	40	40	40	40	40	120	40	40	40	40	40	40
Diameter of specular roll(m)	0.5	0.5	0.5	0.5	0.2	1.0	0.3	0.5	0.5	0.5	-	0.5	0.5
Temperature of specular roll(℃)	50	50	50	50	50	50	50	50	50	120	50	50	50

Note: UV means ultraviolet ray.

Table 3

	Example							Comparative Example					
	1	2	3	4	5	6	7	1	2	3	4	5	6
Glossiness(%)	60	40	65	35	45	55	55	15	8	10	10	15	15
Adhering area ratio(%)	1.5	4.0	1.5	2.5	2.7	2.2	1.5	5.5	7.0	6.5	6.5	0.05	6.5
Failure of perforation(%)	0.2	1.2	0.5	0.8	0.9	0.7	0.6	5.5	13.5	7.5	7.5	0.1	7.5
Printing endurance	○	○	○	○	○	○	○	○	○	○	○	X	○
Quality of image	○	○	○	○	○	○	○	△	X	X	X	○	X
Curling	○	○	○	○	○	○	○	○	○	X	○	○	X
Delamination	○	○	○	○	○	○	○	○	○	○	○	X	○
Wrinkling	○	○	○	○	○	○	○	X	○	X	○	○	○

[0050] Comparison of Examples 1 and 2 with Comparative Example 4 shows that stencil sheets superior in various properties to those of the conventional stencil sheet can be obtained according to the method of the present invention. Comparison of Examples 1 and 2 with Comparative Example 1 shows that when a photo-curable adhesive is used, stencil sheets superior in various properties can be obtained than when a solvent type adhesive is used. Furthermore, comparison of Examples 3 and 4 with Comparative Examples 5 and 6 shows that it is preferred to carry the thermoplastic film and the porous support under a tension of greater than 0.05 kgf and smaller than 7 kgf. Moreover, comparison of Examples 1 and 2 with Comparative Example 2 shows that coating amount of the adhesive is preferably less than 2.0 g/m^2. Moreover, comparison of Examples 1 and 2 with Comparative Example 3 shows that the temperature of the specular roll is preferably lower than 120°C.

[0051] The production conditions according to the present invention vary depending on the kind of the film used, and the like, and, generally, stencil sheets excellent in various properties can be obtained by setting the conditions satisfying the conditions of a glossiness of 30% or more and an adhering area ratio of 0.1-5% in accordance with Table 3.

[0052] According to the present invention, there is provided a heat-sensitive stencil sheet comprising a thermoplastic film and a porous support which are laminated with adhesives wherein glossiness indicating the smoothness of the film surface is 30% or higher and adhering area ratio is 0.1-5%. Therefore, even when perforation is carried out by a high resolution thermal head such as of 600 dpi, there can be obtained a heat-sensitive stencil sheet which is not only free from failure in perforation caused by unevenness of the film surface of the heat-sensitive stencil sheet and failure in perforation on the film surface caused by puddles of adhesives between the fibers of the porous support, but also is high in adhesive strength between the porous support and the thermoplastic film and excellent in printing endurance.

[0053] The heat-sensitive stencil sheet of the present invention can be produced by allowing a thermoplastic film coated with a photo-curable adhesive on one side to closely contact with an outer surface of a porous support previously allowed to be held in close contact with a specular roll, and moving them together during which the adhesive is cured by irradiation with light on the specular roll to laminate the thermoplastic film and the porous support. Since the photo-curable adhesive comprises a photo-curable resin of solventless one-pack type, the working environment is not polluted, the stencil sheets can be produced at high speed in a short time, and, furthermore, since the adhesive does not change in its viscosity during suspension of the production line, not only excellent productivity can be ensured, but also superposition and adhesion of the porous support and the thermoplastic film can be simultaneously performed on the specular roll, and thus the passing lines of the porous support and the thermoplastic film can be shortened and the productive facilities can be made smaller. Moreover, the passing lines of the porous support and the thermoplastic film are short and the carrying tension can be made lower. Therefore, failure of passing and formation of wrinkles are less, and, besides, heat-sensitive stencil sheets excellent in carrying operation, less in curling, and stable in quality can be produced.

Claims

1. A heat-sensitive stencil sheet comprising a thermoplastic film and a porous support which are laminated to each other with an adhesive, in which glossiness as an indication of smoothness of the film surface is 30% or higher and adhering area ratio is 0.1-5%.

2. A heat-sensitive stencil sheet according to claim 1, wherein the thermoplastic film has a thickness of 2 μm or less.

3. A method for producing a heat-sensitive stencil sheet comprising a thermoplastic film and a porous support laminated to each other with an adhesive, which comprises carrying a porous support in close contact with the surface of a specular roll under a given carrying tension while carrying a thermoplastic film coated with a given amount of a photo-curable adhesive on one side under a given carrying tension, allowing the thermoplastic film to closely contact with the outer surface of the porous film on the specular roll with the adhesive being present between the thermoplastic film and the porous support whereby the thermoplastic film and the porous support are moved together, and curing the adhesive by irradiation with light above the specular roll.

4. A method according to claim 3, wherein the thermoplastic film and the porous support are carried under a carrying tension of 0.1-5 kgf.

5. A method according to claim 3, wherein the coating amount of the adhesive is 0.05-1.0 g/m^2.

6. A method according to claim 3, wherein the diameter of the specular roll is 0.1-1.5 m.

7. A method according to claim 3, wherein the specular roll is kept at a temperature of 15-90°C.

8. A method according to claim 3, wherein the thermoplastic film has a thickness of 2 μm or less.

FIG. 1

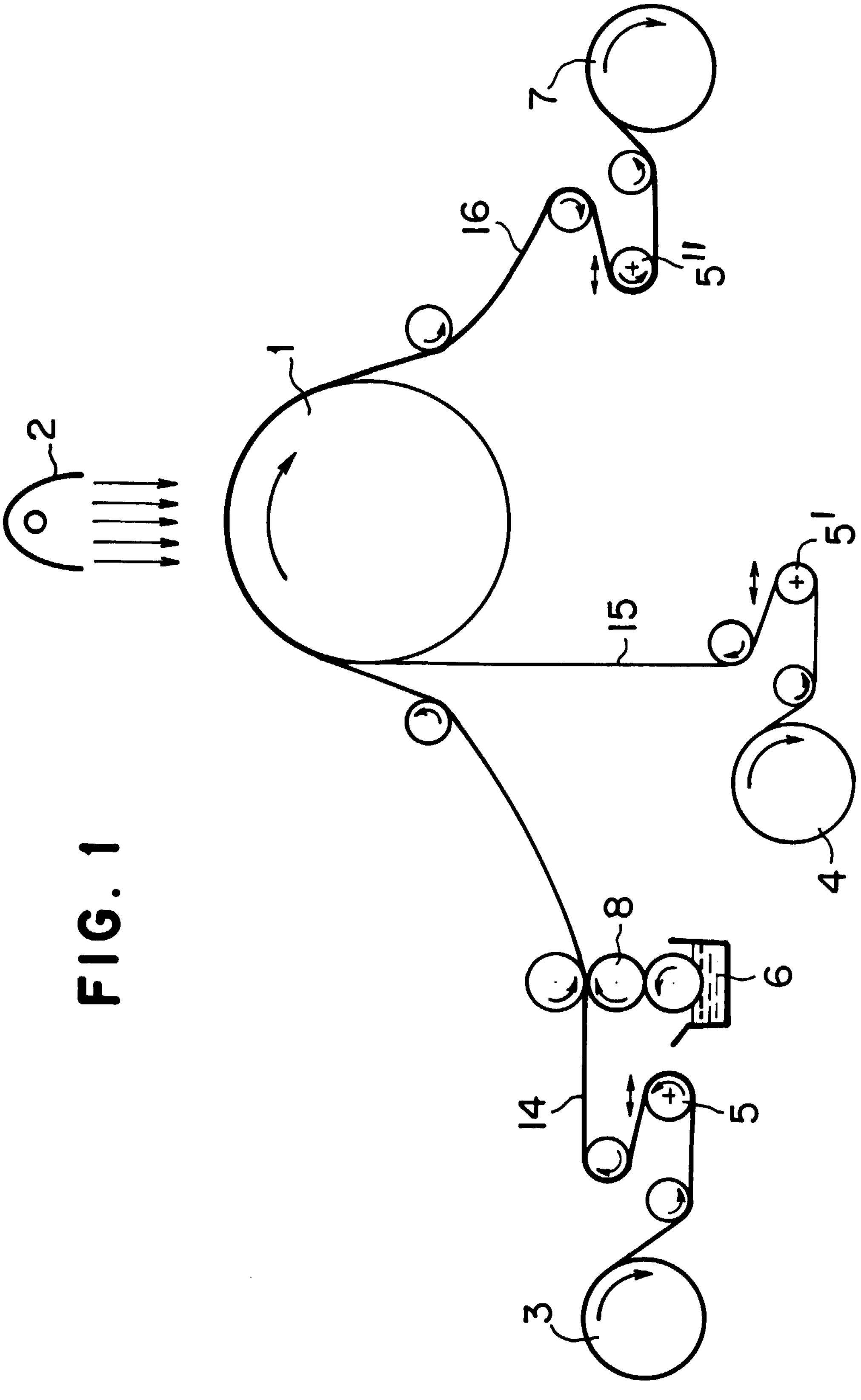

FIG. 2

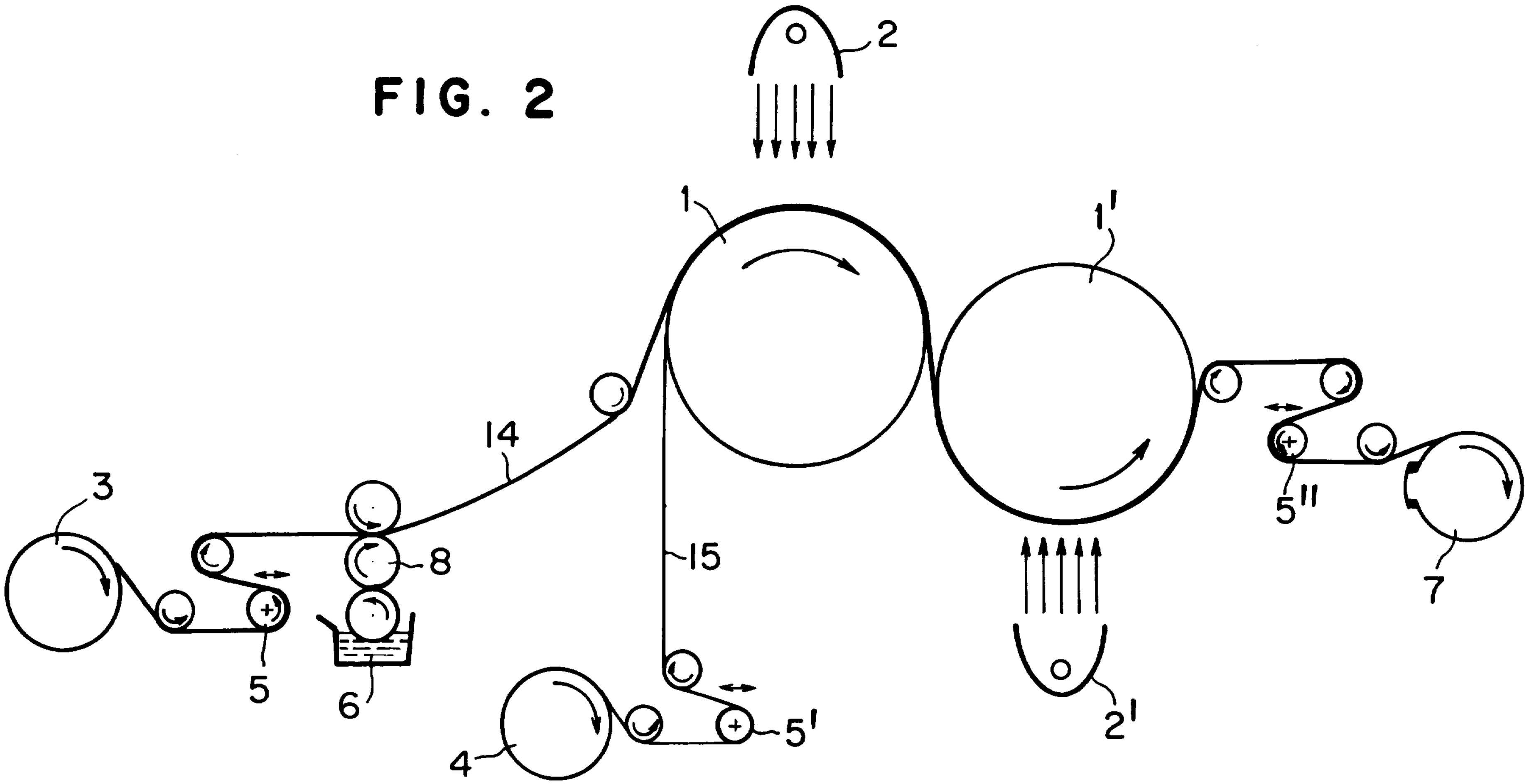

FIG. 3

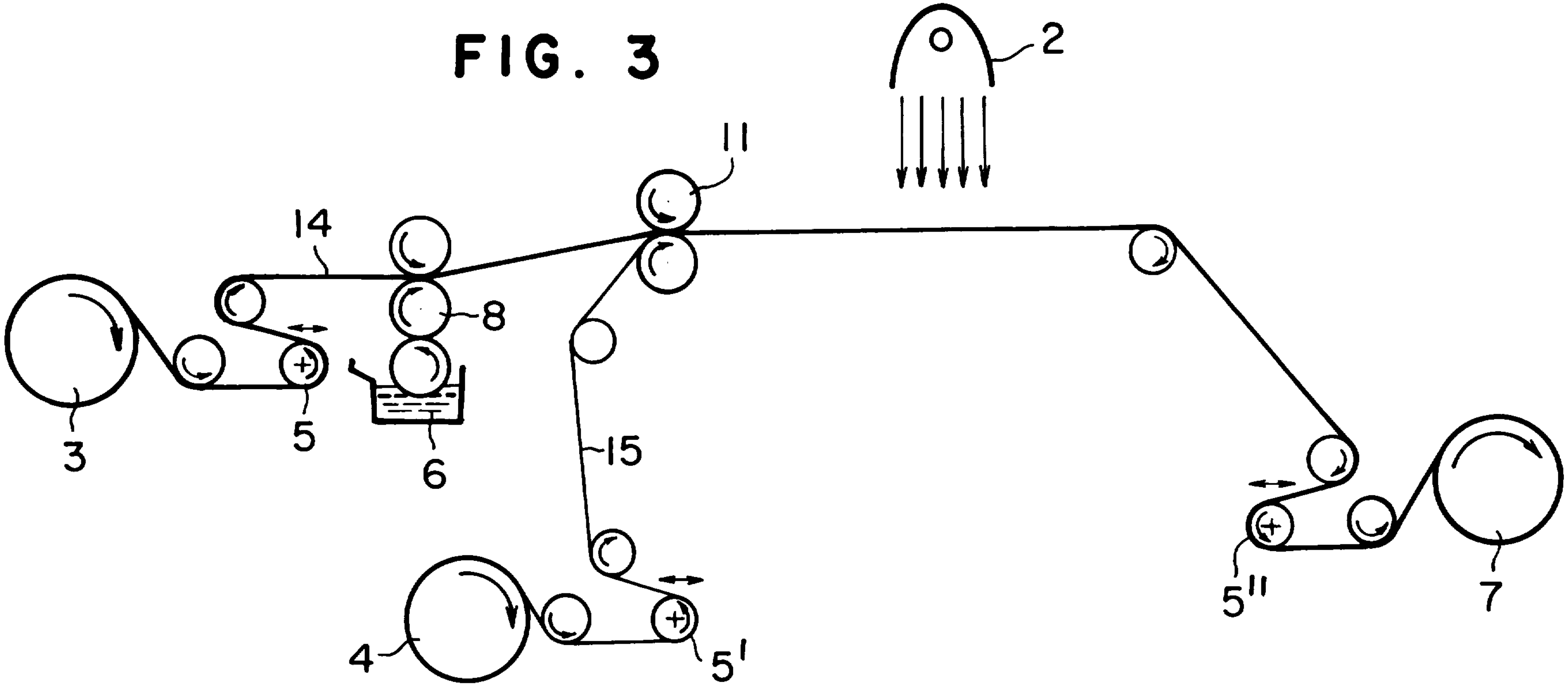

FIG. 4

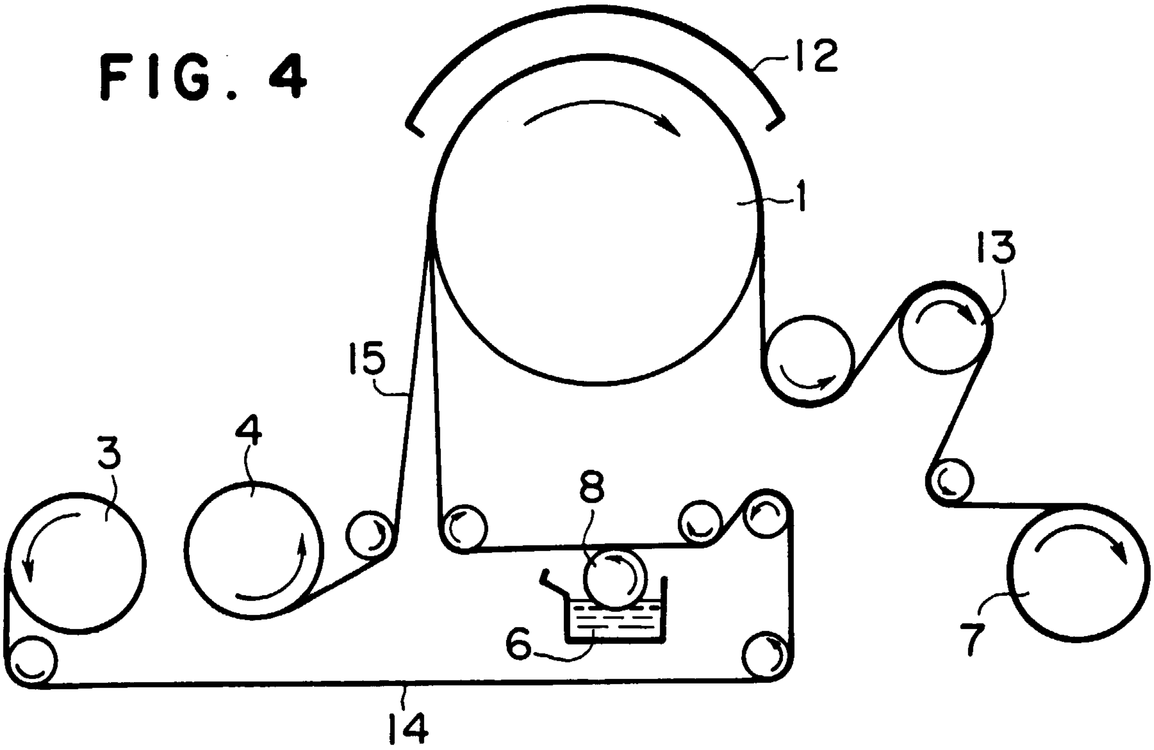

FIG. 5