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HALF-TONE PRINTING MEMBERS AND METHOD FOR MAKING SAME

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This invention relates to printing members and methods for producing these members. More particularly, the invention relates to printing members having the ability to produce half-tone imprints in a single step and to a method of making these printing members.

The photographic process is an old one having been made available to the public in the year 1839. Photo engraving, which is the generic term applied chiefly to the making of etched metal printing plates or blocks of zinc, copper, brass, etc., the design being in relief for topographical printing, is of more recent origin.

Since half-tone photoengraving techniques are used in the present invention, this art will be discussed briefly. Half-tone engraving represents a major phase of photoengraving art. It is the process by which full tone subjects are reproduced to create the impression of a real life view. A photographic negative is made in the usual way, but to produce an etched surface on the printing member, the exposure is made through a screen. This screen may be composed of grains in the case of a mezzograph, or more generally, a series of lines running across each other at right angles. The cross-lined screen usually consists of two sheets of thin plate glass ruled with diagonal lines of mechanical exactitude. These are engraved into the glass, each piece of glass being ruled at right angles to the other. The lines are filled with a black pigment, leaving transparent spaces between them. The two sheets of glass are placed face to face and sealed, the black lines crossing each other and leaving square transparent openings through which the light passes, forming a half-tone or dot image on the photographic film or plate. The screen is interposed between the photographic plate in the camera and the object to be photographed. When the negative is developed, the tones in the original object are represented by a number of dots varying in area according to the tones of the original object. Black areas exist where the original object was white, and conversely, where the original object was dark, the negative will be transparent allowing light to pass through without hindrance.

From the half-tone negative a printing plate is prepared from a metal such as copper, zinc, brass, magnesium, or any other readily etchable material. This is accomplished by interposing the half-tone negative between a bright light (usually an electric arc) and the metal plate. The metal plate has been coated with a light sensitive solution which, as those skilled in the art will appreciate, may be of varied compositions. When the metal plate consists of copper, the light sensitive solution frequently is composed of water, fish glue and ammonium bicarbonate. Zinc plates are usually coated with a solution of ammonium bicarbonate and shellac in an alcohol carrier. This light sensitive solution is poured onto the plate which is usually placed in a whirler to distribute the coating evenly. The time of exposure varies according to the density of the negative, the solution used, and the intensity of the light. The coating is hardened in the areas where the light penetrates the negative and strikes the coating. The coating which is not hardened is readily washed away with an alcohol or other appropriate solvent.

The plate is then placed in an etching bath which, in the case of copper, usually consists of iron perchloride, or in the case of zinc, dilute nitric acid. The exposed portions of the plate not protected by the hardened light sensitive film are etched until the fine "dots" in the highlights (lighter portions of the final printing plate) are as small as it is possible to etch them without undercutting or losing the "dots." The degree of etching is proportional to the time the plate is allowed to remain in the acid bath. The resultant plate now has a relief design of the original photograph image with the etched surfaces duplicating the areas in the negative which were opaque to light while the unetched areas duplicate the transparent areas of the negative. In those areas which were broken into dots by the screen interposed between the negative and object photographed, the surface forms a dot pattern of the original object in positive relief. This forms a master mold which may be used directly in printing, but which is used in the present invention to form a somewhat less durable negative mold or series of negative molds from which are cast the resilient printing members of the present invention.

The negative mold is prepared by molding a thermoplastic resin or thermosetting resin upon the surface of the master mold. If a thermoplastic resin is used, it should have a melting point in excess of that which is necessary in the heating step required to form the microporous microreticulated resin hereinafter discussed. This thermoplastic or thermosetting resin becomes fixed about the master positive mold in a close fitting relationship so that all of the characteristics of the positive mold appear on the superimposed resin in negative relief. For this purpose a phenol-formaldehyde resin on a paper backing in an intermediate stage of polymerization is very suitable. It is responsive to heat and pressure during the molding operation, but is converted thereby to a thermoset stage of polymerization. As such, it is not affected by heating steps required in the practice of the present invention.

It is from a negative mold of the type mentioned above that many printing members have been prepared in the past. For example, printing members containing half-tone reliefs have been made from negative molds by casting thereupon a continuous sheet of vulcanizable material such as natural or synthetic rubber. As heat and pressure are applied to the rubber, it takes shape about the relief pattern of the negative mold so that the two conform reasonably well with each other. This process has been used extensively in producing hand stamps and line cuts in rubber stamps. Limited utilization has been made of the method for producing half-tone printing members bearing images of human beings, scenery and the like. The process and printing members have not enjoyed much success, however, due to the problems encountered in inking them. In order to make an imprint having great detail and good contrasts, frequently referred to as high fidelity, it is necessary not only that the printing member itself be flawless, but that it be inked in a very precise manner. Each of the hundreds of raised portions or dots on the half-tone printing member must be inked evenly. The areas between the raised dots must not contain ink that can be transposed to paper or other surfaces upon which an imprint is made, for such excess ink will cause blotting and loss of detail. Proper inking can be accomplished only by the use of an ink pad equipped with an extremely fine covering for metering the ink to the half-tone printing member upon each inking of the printing member. Obviously, the viscosity of the ink, its pigment, etc. become quite critical in an ink pad of this kind. Even when extreme care is exercised and good materials used, the results are seldom satisfactory.

An object of the present invention is an improvement in the method of making printing members capable of producing half-tone imprints having greater fidelity than is possible using a conventional rubber stamp in conjunction with photoengraving processes, and which do not require inking. Another object of the invention is an improved resilient printing member capable of producing half-tone imprints of high fidelity without inking from an ink pad.

The above objects and others which will be recognized are accomplished by the present invention which consists of a printing member having a half-tone relief on the surface thereof, the half-tone surface having a microporous microreticulated resinous structure, the pores of which are filled with a printing fluid which is expressed only upon the application of pressure. The half-tone printing member is formed by filling or surfacing the face of a negative mold of the type heretofore discussed with a plastisol containing ink, and heating the plastisol until a microporous microreticulated resinous half-tone printing surface is formed, the pores of the microporous surface containing a printing fluid.

The word "plastisol" when used alone herein is intended to mean a conventional plastisol or organosol. Such plastisols are finely divided or colloidal dispersions of a synthetic resin or mixture of resins in a plasticizer or plasticizers with or without other materials such as stabilizers and the like. When heated, the plasticizer and solvents penetrate the resin or volatilize and the mixture sets by coalescence and subsequent solidification of the resin particles. Plastisols are conventionally used for molding, casting films, coating or printing with the resin itself as a coloring agent or coloring carrying agent. The term "ink-containing plastisol" as used herein means a special kind of plastisol. It is a plastisol which when heated will produce a microporous microreticulated resinous structure, the pores of which contain a fluid carrying coloring matter. Its chemical composition may be considerably varied. Preferably, it is composed of a finely divided thermoplastic resin or thermosetting resin in the thermosplastic stage of polymerization, a plasticizer for the resin and a color carrying liquid which is a relative non-solvent for the resin. The non-solvent liquid, having dissolved or dispersed therein a dye or other suitable coloring agent, constitutes the "ink." When an ink-containing plastisol of the above type is heated to a temperature above the softening point of the resin while, if necessary, maintaining a sufficient pressure to retain the non-solvent in the system, a microporous microreticulated structure is formed. The words "microporous microreticulated" are intended to mean that the resinous structure contains many pores which are invisible to the eye and that these pores open upon the surface of the resin which carries the half-tone pattern.

Mixtures of thermoplastic resins, plasticizers and non-solvents for the resins may be used. In addition, there may be used a combination of plasticizers, one or more of which has a greater solvency or plasticizing effect on the resin than the other. It will be appreciated that the terms solvents, plasticizers and non-solvents are relative terms. A liquid which may be a non-solvent for one resin may be a plasticizer for another. Although a liquid may act as a partial plasticizer for a resin, it may still serve the function of a non-solvent in a resin-plasticizer-non-solvent combination mentioned above. Thus, a resin and a plurality of plasticizers, one of which may be considered a primary plasticizer and one of the others a secondary plasticizer, may be used to prepare the "ink-containing plastisol" of the invention. Similarly, it is possible to combine a resin and a plasticizer in combinations such that a portion of the plasticizer serves as a plasticizer and the remainder a non-solvent as that term is used herein. This resin-plasticizer combination is not nearly as desirable as those discussed earlier, but is intended to be embraced by the present invention. A secondary plasticizer is a plasticizer which has limited compatibility with the resin. It usually dilutes the primary or secondary plasticizer, thus reducing its ability to soften the resin. This is a valuable phenomena since it permits the use of many plasticizers whose compatibility with the resin would otherwise be excessive.

In the formation of the microporous microreticulated resin herein contemplated, the structure is formed by the partial coalescence of the resin particles. The resin particles become bonded at their surfaces forming an innerconnecting network of microscopic pores which extend throughout the resinous structure and communicate with its surface. The non-solvent for the resin and perhaps a portion of the plasticizer remains in the voids between the partially coalesced resin particles, filling the pore network thus formed. Likewise, when an excess of plasticizer or a combination of primary and secondary plasticizers are employed beyond the maximum absorbable by the resin, this portion of the plasticizer or plasticizers does not penetrate the resin, but remains in the pore network to form, with coloring matter, the "ink" of the half-tone printing members of the present invention.

It will be appreciated that the softening points of many synthetic resins are lowered in the presence of various plasticizers, so that exact molding temperatures cannot be given, but will depend upon the particular mixture of plasticizer and resin. The time required will range from a few seconds to about one hour.

Any thermoplastic resin or thermosetting resin in the thermoplastic stage of polymerization may be used in the preparation of the "ink-containing plastisol." The synthetic resin will constitute a substantial portion of the composition, but as little as 15% of the composition may consist of resin. The maximum amount of ink which is consistent with a strong structure is desired. Usually, the resin content will vary from about 15 to about 65 percent by weight of the ink-containing plastisol; about 20 to about 50 percent being preferred. Typical synthetic resins are cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polymethyl methacrylate, polymethyl acrylate, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl butyral, polyvinyl acetate, copolymers of vinyl chloride and vinyl acetate, polyamides, such as poly e-caprolactam, polyhexamethylene adipamide, copolymers of adipic acid, sebacic acid, e-caprolactam and hexamethylene diamine, polyisocyanates, otherwise known as polyurethane resins, such as the polyesters of 2,4-tolylene diisocyanate and polyethylene adipate, polyethylene, polypropylene, polyacrylonitrile, polymethylstyrene, alkyd resins, such as polymers of phthalic acid and ethylene glycol, polyesters of ethylene glycol and terephthalic acid, polyesters of ethylene glycol, terephthalic acid and acrylonitrile, thermoplastic epoxy resins, such as condensation products of epichlorohydrin and polyhydroxy compounds, such as 2,2-bis-(4-hydroxyphenyl)propane. Polyvinyl chloride and copolymers of vinyl chloride and other ethylenically unsaturated monomers are preferred. This list is not complete, and those skilled in the art will appreciate from the above, other synthetic resins which can be employed.

With the thermoplastic resins, there will be used a plasticizer for the resin. Many such plasticizers are known. In the following table there are given many known plasticizers, and the resins with which they are compatible. Again, this list is incomplete, but those skilled in the art will be aware of other plasticizers and can select one which will be satisfactory and available.

PLASTICIZERS

	Compatibility								
	CA	CAB	EC	PM	PS	VA	VB	VC	VCA
Methyl abietate	I	C	C	C	C	I	C	C	C
Di-isooctyl adipate	P	C	C	C	C	C	I	C	C
2-Nitrobiphenyl	C	C	C	C	C	C	C	C	C
Chlorinated biphenyl	I	C	C	------	C	C	C	C	C
Glycerol triacetate	C	C	C	C	----	C	----	----	I
Triethylene glycol di-2-ethylbutyrate	I	C	C	C	----	C	C	C	C
Polyethylene glycol di-2-ethylhexoate	I	------	C	C	----	C	I	C	C
Methyl phthalyl ethyl glycolate	C	C	C	C	C	C	C	C	C
Butyl phthalyl butyl glycolate	C	C	C	C	C	C	C	C	C
Aromatic hydrocarbon condensate	P	P	C	C	C	C	C	C	C
Ethylene glycol mono-butyl ether laurate	----	C	C	------	C	----	C	C	C
Tetrahydrofurfuryl oleate	P	C	C	C	C	C	----	C	C
Pentaerythritol tetra-propionate	C	C	C	------	C	C	C	C	C
Cresyl diphenyl phosphate	P	C	C	------	I	I	C	C	C
Tricresyl phosphate	C	C	C	P	C	C	C	C	C
Dimethyl phthalate	C	C	C	C	C	C	C	P	C
Diethyl phthalate	C	C	C	C	C	C	C	P	C
Di-n-octyl phthalate	I	C	C	C	C	I	C	C	C
Di-isooctyl phthalate	I	P	C	C	P	C	P	C	C
Di-2-ethyl phthalate	I	C	C	C	C	I	P	C	C
Butyl ricinoleate	I	C	C	------	P	C	C	I	C
Dibutyl sebacate	I	C	C	C	C	C	C	C	C
Ethylene glycol mono-butyl ether stearate	I	P	C	------	P	P	C	P	C

C=compatibility.
P=partially compatible.
I=incompatible.
CA=cellulose acetate.
CAB=cellulose acetate butyrate.
EC=ethyl cellulose.
PM=polymethyl methacrylate.
PS=polystyrene.
VA=polyvinyl acetate.
VB=polyvinyl butyral.
VC=polyvinyl chloride.
VCA=polyvinyl chloride acetate.

Primary plasticizers which have been successfully used are tricresyl phosphate, dioctyl phthalate, polyethylene glycol benzoate, dibutyl phthalate, alkyl aryl phosphates and glycolates. Secondary plasticizers which have been used in varying amounts are fatty acid esters and aromatic hydrocarbon distillates such as those boiling at a temperature of 300–450° F.

The plasticizer will usually be used in an amount within the range from about 40 to about 170% by weight of the resin.

This nonsolvent can be either volatile or nonvolatile. The more volatile the nonsolvent, the greater the pressure that will have to be exerted to retain the solvent in the mixture until the structure has been formed. But since the final structure of the present invention is to contain an ink, it is desirable to use a nonvolatile liquid to avoid drying out of the structure during long periods of nonuse.

Those skilled in the art with the above facts will be able to select appropriate nonsolvents. The nonsolvents useful for the various resins which are disclosed above will be apparent to those skilled in the art from these facts. However, the following list which is partial, will give some indication of nonsolvent liquids which can be employed in the invention.

LIST OF NONSOLVENTS

	Solvency								
	CA	CAB	EC	PM	PS	VA	VB	VC	VCA
n-Butyl alcohol	I	I	S	I	I	S	S	I	I
Isoamyl alcohol	I	I	S	I	I	I	I	I	I
n-Hexyl alcohol	I	I	----	------	------	I	S	I	I
2-Ethylhexyl alcohol.	I	I	----	------	------	S(W)	S	I	I
Sec,heptadecyl alcohol.	I	I	----	------	------	I	I	I	I
4-tert-Amylcyclohexanol.	I	I	P	P	P	------	P	I	I
Glycol diacetate	S	S	----	------	------	S	I	I	P
Butyl lactate	I	S	S	S	------	S	----	I	S
n-Butyl ether	I	I	----	------	------	I	I	I	I
Ethylene glycol mono-n-hexyl ether.	----	------	----	------	------	------	----	----	------
Diethylene glycol monoethyl ether.	I	I	----	------	------	S	S	I	I
Terpene methyl ethers.	I	I	S	P	I	I	P	----	------
2-Methyl tetrahydrofuran.	S	------	S	P	S	S	P	P	S
Ethylene Glycol	I	I	I	I	I	I	I	I	I
1,2-Propylene glycol.	I	I	I	I	I	I	I	I	I
1,3-Butylene glycol	I	I	I	I	I	I	I	I	I
2-Methyl-2,4-pentanediol.	I	I	S	I	I	I	I	I	I
Diethylene glycol	I	I	I	I	I	I	I	I	I
Diethylene glycol monoricinoleate.	I	I	S	I	I	I	I	I	I
Triethylene glycol	I	I	I	I	I	I	I	I	I
Polyethylene glycol.	I	I	I	I	I	I	I	I	I
Polypropylene glycol.	I	I	I	I	I	I	I	I	I
Thiodiethylene glycol.	I	I	I	I	I	I	I	I	I
Amyl chlorides, mixed.	I	I	S	I	S	------	I	I	I
Glycerol monoricinoleate.	I	I	S	I	I	I	I	I	I
Chloroform	S	S	S	S	S	P	S	P	P
Cyclohexane	I	I	I	I	S(W)	I	I	I	I
Xylene (Ortho, Meta, Para.)	I	I	S	S	S	S	S	I	S
Diamylbenzene	I	I	I	I	P	------	I	I	I
Amylnaphthalene	I	I	P	I	P	------	I	I	I
Petroleum ether (light ligroin).	I	I	I	I	I	I	I	I	I
Gasoline (Benzine)	I	I	I	I	I	I	I	I	I
Ligroin (Petroleum naphtha.	I	I	I	I	I	I	I	I	I
Aliphatic petroleum naphtha.	I	I	I	I	I	I	I	I	I
V.M. and P. Naphtha.	I	I	I	I	I	I	I	I	I
Stoddard solvent (White spirits) (Safety solvent).	I	I	I	I	I	I	I	I	I
Mineral spirit (Heavy naphtha.	I	I	I	I	I	I	I	I	I
Mineral oil	P	P	P	P	------	P	P	I	P
Petroleum spirits	I	I	I	I	I	I	I	I	I
Kerosene (Fifth fraction of petroleum.	I	I	I	I	I	I	I	I	I
Nitromethane	S	S	I	------	------	S	----	I	I

S=soluble.
P=partially soluble.
L=latent or co-solvent.
I=insoluble.
W=warm.
CA=cellulose acetate.
CAB=cellulose acetate butyrate.
EC=ethyl cellulose.
PS=polystyrene.
PM=polymethyl methacrylate.
VC=polyvinyl chloride.
VCA=polyvinyl chloride acetate.

A wide variety of coloring matter may be used including both dyes and pigments. Satisfactory pigments include the phthalocyanine blues and greens, ink type carbon blacks and B-oxynaphthoic acid reds. Satisfactory dyes include methyl violet, victoria blue, victoria green, azosol red, calcazine red, iosol red and nigrosine blacks. Both fluorescent and phosphorescent dyes and pigments may be used.

Half-tone screens exist in various "gratings" or rulings ranging from 40 to 400 lines to the inch. In the printing of most paper of the newspaper variety, a 60 line screen is usually employed. For ordinary black and white commercial work, screens from 120 to 150 mesh are used. The still finer screens are used for fine color reproductions. Any of the available screens ranging from 40 to

400 lines to the inch may be used in the present invention, since the thermoplastic resin powder when heated will conform to the half-tone depressions of the negative mold leaving pores communicating from the interior of the microporous resin to the protrusions or dots comprising the surface of the half-tone printing member. The resin powder should not be larger than about 75 mesh and not smaller than about 600 mesh. Preferably, and for most printing members, the screen will contain from about 40 to about 150 lines per inch and a majority of the resin particles by weight will be between 400 and 100 mesh size.

Having generally described the invention, the following examples and comparisons are presented as specific embodiments only and without intending to limit the invention thereto.

(A) *Preparation of Negative Mold*

A photograph of a picture of the President of the United States was taken through a 60 line screen. When developed by standard procedures, the negative had black areas where the original photograph was white and conversely, where the original photograph was black the negative was transparent. The transparent lines criss-crossed the negative, duplicating the screen. The negative was superimposed over a zinc plate which had been coated with a solution of ammonium bicarbonate and shellac in alcohol. The assembled negative and sensitized zinc plate were then subjected to light from a carbon arc lamp. The light which passed through the transparent areas of the negative hardened corresponding areas of the bichromate and shell coating of the zinc plate. Those areas of the coating which were covered by the opaque areas of the negative did not receive light and were not hardened. Subsequently, the metal plate was washed in methyl alcohol removing the unhardened areas of the coating, leaving behind the hardened areas in duplication of the original picture. The plate was then placed in an etching solution of nitric acid and left for a period of approximately 30 minutes. The exposed areas of the metal became etched by the nitric acid, reducing the metal plate to a relief design of the original photograph image with the etched surface duplicating the areas in the negative which were opaque to light while the unetched areas duplicated the transparent areas of the negative. In the areas which were etched, the surface was a dot pattern of the original photograph in relief. Upon this master positive metal mold, a Bakelite composition of an intermediate stage phenol formaldehyde resin on a paper backing was impressed to produce a negative mold.

EXAMPLE 1

50 parts of Geon 121, a polyvinyl chloride powder all of which will pass through a 200 mesh screen, and 5 parts of tribasic lead sulfate (a stabilizer) were mixed with 50 parts of dioctyl phthalate to form a paste. To this paste was added 5 parts of methyl violet together with 50 parts of glycerol monoricinoleate, serving as a vehicle therefor. This "ink-containing plastisol" was poured into the negative mold of Example A. The mold was placed in a 300° F. oven and heated for about 25 minutes. Thereafter the mold was removed from the oven, cooled, and the resultant printing member stripped from the mold. The printing member, which carried the photograph in fine detail, was glued to a conventional wood hand stamp handle and used to make several thousand imprints. Each imprint represented a highly faithful reproduction of the details of the original photograph including the lighting effect, hairline and various shades of clothing. Individual half-tone "dots" were readily discernible throughout the image.

EXAMPLE 2

Example 1 was repeated using a negative mold produced in accordance with Example A, except that it possessed 100 gratings (half-tone lines) per inch. The finished printing member produced half-tone imprints of high fidelity. The half-tone dots were independently visible on the printing member and did not bleed into each other on imprints made with the member.

EXAMPLE 3

Example 1 was repeated using a polyvinyl chloride powder passed through a 75 mesh screen and retained on a 100 mesh screen. The finished printing member produced reasonably satisfactory half-tone imprints, but showed some evidence of irregularities in the half-tone areas. This indicates that a mesh size greater than 75 would be desirable for use in the invention.

EXAMPLE 4

Example 1 was repeated substituting 25 parts of an aromatic petroleum distillate having a boiling range of 380–400° F. (a secondary plasticizer for polyvinyl chloride) for one-half of the dioctyl phthalate. A stamp of comparable quality was obtained.

EXAMPLE 5

50 parts by weight of a 200 mesh thermoplastic resin having the composition of 87% vinyl chloride, 13% vinyl acetate and 5 parts of tribasic lead sulfate were mixed with 30 parts of tricresyl phosphate, 30 parts of an aromatic petroleum distillate having a boiling range of 380–400° F. and 40 parts of 2-ethylhexanediol-1,3 with which there had been added 5 parts of methyl violet. The resulting ink-containing plastisol was poured into the negative mold of Example A. The mold was placed in an oven at 300° F. for 20 minutes. After cooling, the printing member was stripped from the mold, inspected, mounted on a handle, and used to produce hundreds of imprints, each representing a faithful reproduction of the original photograph. As in Examples 1, 2 and 4, there was no smudging of the impression caused by excessive inking as is so frequently the case with conventional half-tone printing members.

(B) *Comparison With Conventional Half-Tone Printing Member*

A conventional rubber picture stamp was made by impressing upon the negative mold of Example A, a layer of natural rubber ⅛-inch thick at a pressure of 30 tons per square inch for 6 minutes at 310° F. Thereafter, the rubber was removed from the mold, trimmed and glued to a wood handle. To the naked eye the printing member carried a reasonably faithful reproduction of the negative mold in half-tone relief. However, it proved to be very difficult to ink due to surface irregularities of the stamp pad and many contacts with a Carters' ink pad was necessary before all of the surface of the stamp was inked. Complete inking was most readily obtained by sliding the face of the printing member across the surface of the ink pad. Often the tiny pockets between the "dots" in the half-tone relief became clogged with ink, making a blur on the imprint. The fidelity of imprints made with the member was not as great as with the half-tone printing members of the present invention described in earlier examples. The present printing members are always inked with just the right amount of ink. The ink is emitted from the interior of the porous structure only under compression or upon being brought into contact with an absorbent material. There is no excess ink on the half-tone surface to clog the minute spaces between the dots.

It is claimed and desired to secure by Letters Patent:

1. A method of making a printing member capable of producing a half-tone imprint which comprises surfacing a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said plastisol comprising (A) from about 15% to about 65% by weight of a thermoplastic resin powder and (B) from about 35% to about 85% by weight of a plasticizer for the resin and a color

carrying liquid which is a nonsolvent for the resin, the plasticizer of (B) being present in an amount equal to at least about 5% by weight of said plastisol; and heating said plastisol to a temperature sufficient to form a microporous resin having a half-tone printing surface, said microporous resin having pores extending throughout the half-tone printing surface and communicating with the interior of said microporous resin, the pores of said microporous resin having disposed therein a printing fluid comprising said color carrying liquid.

2. A process in accordance with claim 1 wherein said thermoplastic resin powder is polyvinyl chloride.

3. A process in accordance with claim 1 wherein said thermoplastic resin is a copolymer of polyvinyl chloride and another ethylenically unsaturated monomer.

4. A method of making a printing member capable of producing a half-tone imprint which comprises surfacing a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said plastisol comprising (A) from about 15% to about 65% by weight of a thermoplastic resin powder of from about 600 to about 75 mesh size, and (B) from about 35% to about 85% by weight of a plasticizer for the resin and a color carrying liquid which is a nonsolvent for the resin, the plasticizer of (B) being present in an amount equal to at least about 5% by weight of said plastisol; and heating said plastisol to a temperature sufficient to form a microporous resin having a half-tone printing surface, said microporous resin having pores extending throughout the half-tone printing surface and communicating with the interior of said microporous resin, the pores of said microporous resin having disposed therein a printing fluid.

5. A method of making a printing member capable of producing a half-tone imprint which comprises surfacing a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said plastisol comprising (A) from about 15% to about 65% by weight of a thermoplastic resin powder, and (B) from about 35% to about 85% by weight of a plasticizer for the resin and a color carrying liquid which is a nonsolvent for the resin, the plasticizer of (B) being present in an amount equal to at least about 5% by weight of said plastisol, said half-tone printing surface being defined by a grid having from about 40 to about 400 lines per inch; and heating said plastisol to a temperature sufficient to form a microporous resin having a half-tone printing surface, said microporous resin having pores extending throughout the half-tone printing surface and communicating with the interior of said microporous resin, the pores of said microporous resin having disposed therein an ink.

6. A method of making a printing member capable of producing a half-tone imprint which comprises covering the surface of a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said half-tone printing surface being defined by a grid having from about 40 to about 400 lines per inch and said plastisol comprising (A) from about 15% to about 65% by weight of a thermoplastic resin powder of from about 600 to about 75 mesh size, and (B) from about 35% to about 85% by weight of a plasticizer for said resin and a color carrying liquid which is nonsolvent for said resin, the plasticizer of (B) being present in an amount equal to at least about 5% by weight of said plastisol; and heating said plastisol to a temperature sufficient to form a microporous resin containing a half-tone printing surface, said microporous resin having pores extending throughout the half-tone printing surface and communicating with the interior of said microporous resin, the pores of said microporous resin having disposed therein an ink.

7. A method of making a printing member capable of producing a half-tone imprint which comprises surfacing a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said half-tone printing surface being defined by a grid having from about 40 to about 150 lines per inch, said plastisol comprising (A) from about 15% to about 65% by weight of a thermoplastic resin powder of from about 100 to about 400 mesh size, and (B) from about 35% to about 85% by weight of a plasticizer for the resin and a color carrying liquid which is a nonsolvent for the resin, the plasticizer of (B) being present in an amount equal to at least about 5% by weight of the plastisol; and heating said plastisol to a temperature sufficient to bond said resin particles together forming a cohesive microporous structure having a half-tone printing surface, the pores of said microporous structure communicating from the interior of said structure to its half-tone printing surface.

8. A method of making a printing member capable of producing a half-tone imprint which comprises surfacing a negative mold having a printing surface in half-tone relief with a plastisol without the use of pressure, vacuum, or wetting agents, said half-tone printing surface being defined by a grid of from about 40 to about 150 lines per inch, said plastisol comprising (A) from about 20% to about 50% by weight of a thermoplastic resin powder of from about 100 to about 400 mesh size, and (B) from about 50% to about 80% by weight of a plasticizer for the resin and a color carrying liquid which is a nonsolvent for the resin, the plasticizer of (B) being present in an amount equal to at least about 8% by weight of the plastisol; and heating said plastisol to a temperature sufficient to bond said resin particles together forming a cohesive microporous structure having a half-tone printing surface, the pores of said microporous structure communicating from the interior of said structure to its printing surface.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,141,407 July 21, 1964

Harry R. Leeds

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, in the table, under the heading "PLASTICIZERS" first column, line 29 thereof, for "Di-2-ethyl phthalate" read -- Di-2-ethylhexyl phthalate --; same column 5, line 41, for "C=compatibility" read -- C=compatible --.

Signed and sealed this 17th day of November 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents