Aug. 27, 1963 H. R. LEEDS 3,101,668

PRINTING MEMBERS AND METHOD OF MAKING SAME

Filed March 14, 1960

FIG. 4

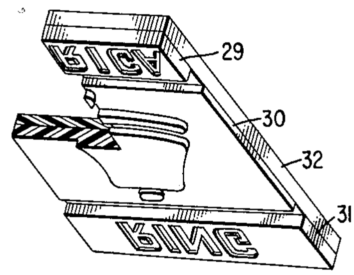


FIG. 1

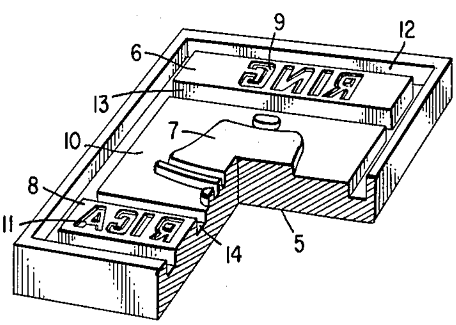


FIG. 2

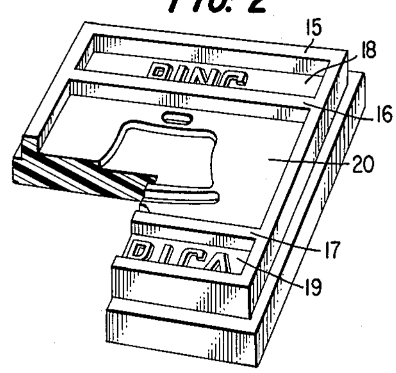
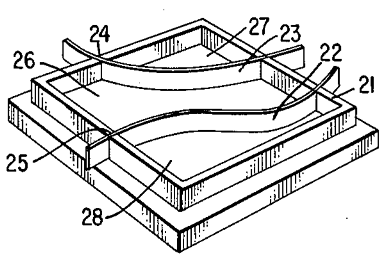


FIG. 3



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PRINTING MEMBERS AND METHOD OF MAKING SAME

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This invention relates to printing members and to methods for producing these members. More particularly, the invention relates to printing members having ink impervious backings, to printing members having the ability to produce multicolored imprints in a single step and to the method of making these printing members.

In the past, printing members containing their own supply of ink have had a tendency to bleed at the backing, particularly when pressure is applied to the printing member to produce an imprint. Bleeding at the backing of the printing member makes it difficult to secure the printing member to supporting means such as hand stamp stocks, metal plates which may be inserted in mechanical equipment for repeated use and the like. Many glues which have been used for fixing printing members carrying their own supply of ink to supporting means are adversely affected by the ink causing deterioration of the bond between the printing member and supporting means.

Further, it has not been possible to make printing members such as hand stamps or other printing plates which are capable of producing imprints of multicolors in a one step operation. Conventional hand stamps must be inked immediately prior to use. This inking operation is accomplished by pressing the printing member of the stamp upon an inked pad. The ink adsorbed by the printing member is then transferred to paper or other surface upon which it is desired to make an imprint by striking the paper with the inked member. Prior to the present invention, multicolored imprints could be produced in such manner by inking a portion of a printing member with one color of ink and subsequently inking the remaining portion with another color, both operations being accomplished prior to striking the surface upon which it is desired to make the imprint. Perhaps also different portions of a printing plate could be inked with different colors by pressing the printing member against an ink pad comprised of sections containing the desired colors, the sections being arranged to engage the appropriate segments of the printing member. In the past, it also may have been possible to produce multicolored imprints by feeding different colored inks from a plurality of ink reservoirs through separate segments of a printing member. In addition, it is well known that in the production of multicolored lithographic work, the several colors are accomplished by independent printing steps. In such a process, great care must be exercised to insure the proper registration of the sheets being printed, this being necessary for the prevention of blurring of the colors at their lines of contact. All of these methods of producing multicolored print are cumbersome and expensive. The printing members and their supporting means are either complex or more than one step is necessary to use them. These difficulties are readily overcome by the present invention.

An object of the invention is a printing member which contains its own ink and does not bleed at its backing.

Another object of the invention is a method of making a printing member containing its own ink supply which does not bleed at its backing.

Another object of the invention is a printing member capable of producing a multicolored imprint in a single operation.

Still another object of the invention is a method of making a printing member containing ink of a plurality of colors with which a multicolored imprint can be produced with a single stroke and without inking the stamp prior to use.

Further objects of the invention will become apparent from the following description and discussion of the invention.

FIGURE 1 is a perspective drawing of a positive mold which may be used in the invention. FIGURE 2 is a perspective drawing of a negative mold used in the invention. FIGURE 3 is a perspective drawing of an alternate negative mold. FIGURE 4 is a perspective drawing of a finished object of the invention. These drawings will be referred to again in the following more detailed description and examples.

In preparing the printing member having an ink impervious backing, a plastisol containing ink is placed in a negative mold, covered with a thermoplastic film and heated to a temperature sufficient to cause the formation of an ink-containing microporous resin bonded to the thermoplastic film. Preferably, the plastisol, containing ink will be placed in a negative mold and heated to a temperature sufficient to gel the plastisol. This gelled plastisol is a partially cured plastisol which differs from the initial plastisol in that it does not flow. Curing is effected by the coalescence of the resin particles at their outer surfaces accompanied by the migration of all or a portion of the plasticizer into the resin. More extended curing results in a microporous structure of substantial strength, the pores being interconnecting and filled with ink. After the plastisol containing ink is gelled, an ink impervious thermoplastic film is superimposed over an exposed portion of the gelled plastisol which contains ink and the complete assembly again heated to form a unitary structure comprising a microporous microreticulated resin filled with ink bonded to an ink impervious thermoplastic sheeting. In situations where printing members containing less flexibility are desired, there may be used in place of the thermoplastic film a composite board comprising paper, cardboard or other fiber impregnated or coated with a thermoplastic resin. The resin coated or impregnated side of the composite board is brought into contact with the gelled plastisol and the assembly heated to form a microporous microreticulated ink containing resin bonded to the composite board. As another desirable alternate, an ink-free plastisol may be poured over the plastisol containing ink in a negative mold such as those depicted in FIGURES 2 and 3. The two layers are then heated to coalesce the two plastisols. The ink-free plastisol becomes an ink impervious thermoplastic layer bound to a microporous resin which is formed from the plastisol containing ink. Preferably, the ink containing plastisol will be preheated to form the gel stage, then covered with the ink-free plastisol and again heated to form the composite structure. This procedure completely eliminates comingling of the two types of plastisols.

In preparing printing members capable of producing multicolored imprints, the cavities of a multicavity negative mold such as those shown in FIGURES 2 and 3 are filled with a plastisol containing ink of the color desired for each segment of the final multicolor printing member. Each cavity of the multicavity mold is separated from the other cavities by barriers. These barriers make it possible to fill the cavities to a depth sufficient to cover the printing characters carried by the negative mold without comingling the colors.

A suitable ink-free backing which holds the variously colored segments of the multicolored printing member in a noncontiguous relationship to prevent comingling of the ink colors and smudging at the lines of contact may take many forms. As discussed earlier, the backing may consist of a sheet of ink impervious thermoplastic resin, a fiber board coated or impregnated with such a resin, or an ink-free plastisol which when heated becomes a thermoplastic or thermoset layer of resin. It also may consist of a liquid impervious cardboard, metal or any other material which is substantially ink impervious and which will maintain the color segments in a noncontiguous relationship. Regardless of the backing selected, the method of preparing the multicolored printing member may include the step of heating the negative mold filled with the plastisol which contains ink to gel the plastisol. This step is particularly helpful when an ink-free plastisol is used in making the backing. The use of a plastisol backing makes it unnecessary to have the plastisols containing different colored inks at the same level in the plurality of cavities of the negative mold prior to the application of the backing. When poured into the negative mold containing the plastisol containing ink, the ink-free plastisol flows into the unfilled portions of the individual cavities bringing the level of the contents of those cavities to the top of the barriers separating the cavities, if the contents are not already at this level. Additional plastisol provides the backing for the final product, joining its several color segments together. Thus, the printing surfaces of the individual segments of the finished multisegment printing member are precisely in the same plane. The preferred preheating step by which the plastisol containing ink is gelled or semicured prevents comingling of the colors as subsequent steps of the process are carried out. This has its greatest importance when ingredients of the two plastisols are compatible with each other, making diffusion of colors expected. In some instances it is desirable to cover the filled mold with a plate or use other means to confine the contents during the final heating step. Such a plate, if securely fixed over the top of the filled mold, prevents undue expansion of the product during heating. It provides a means of regulating the porosity of the composition to some extent. A cover may also be used to retard the evaporation of some of the more volatile components of the plastisol. It provides a means for bringing pressure, due to expansion of the plastisol containing ink, upon the plastic backing to enhance its ability to bond to the microporous resin formed from the plastisol containing ink.

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 thermoplastic 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, constitute 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 are interconnecting.

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. (The resin powder will have a mesh size of between about 75 and about 600, and preferably between about 100 and about 400.) 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-isoctyl 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 monobutyl ether laurate	----	C	C	----	C	----	C	C	C
Tetrahydrofurfuryl oleate	P	C	C	C	C	C	----	C	C
Pentaerythritol tetrapropionate	C	C	C	----	C	C	C	C	C
Cresyl diphenyl phosphate	P	C	C	----	I	I	C	C	C
Tricresyl phosphte	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-ethylhexyl 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 monobutyl ether stearate	I	P	C	----	P	P	C	P	C

C=compatible.
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 wire 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.

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

(A) *Preparation of Multicavity Negative Mold*

A negative mold for preparing a multicolored printing member such as that shown in FIGURE 4 was prepared as follows: A black and white painting of a bell with certain attending printed words was photographed. 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 negative was superimposed over a zinc plate 5 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 **6**, **7**, and **8** of the bichromate and shellac coating of the zinc plate. Those areas of the coating **9**, **10**, and **11** 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 **6**, **7**, and **8**. The plate was then placed in an etching solution of nitric acid and left for a period of approximately 30 minutes. The now uncoated areas **9**, **10**, and **11** 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 surfaces **9**, **10**, and **11** duplicating the areas in the negative which were opaque to light, while the unetched areas **6**, **7**, and **8** duplicated the transparent areas of the negative. A groove **12** was machined around the perimeter of the zinc plate encompassing the bell and accompanying words. Additional grooves **13** and **14** were machined, separating the bell from the words. Upon this master positive metal mold of FIGURE 1, a Bakelite composition consisting of a phenol formaldehyde resin in the thermoplastic stage of polymerization on a paper backing was impressed at an elevated temperature, about 400° F., to produce the three cavity negative mold of FIGURE 2. Upon heating and the application of pressure, the resin takes a position around the characters and design of the positive mold and once set it is not affected by subsequent heating.

It will be noted that the features of the mold of FIGURE 2 are the reverse or negative of the master of positive mold of FIGURE 1. Barriers **15**, **16**, and **17** of FIGURE 2 correspond to grooves **12**, **13**, and **14** of FIGURE 1. These barriers establish color cavities **18**, **19**, and **20**.

Either a thermoplastic or thermosetting resin in the thermoplastic stage of polymerization may be used in the preparation of the negative mold in accordance with the above procedure. 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 ink containing resin of the printing members. The positive mold as well as the negative mold may be prepared in any manner known in the art. The method employed will depend upon the equipment available and the nature of the multicolor printing member desired. The molds may even be carved by hand from wood, metal, rubber or the like. One very desirable alternate method of producing a positive mold is by stripping sections of the rubber facing from a commercially available composite rubber panel containing an embedded fabric. The areas from which the rubber has been stripped serve as recesses corresponding to barriers of a negative mold which may be formed by pressing a thermoplastic resin against it as discussed earlier. A negative mold may be prepared with barriers such as those shown as **21**, **22**, and **23** in FIGURE 3. Barriers **22** and **23** are strips of metal, plastic, cardboard or similar material fitted into slots **24** and **25** of an outer barrier **21** to establish cavities **26**, **27**, and **28**. A very desirable substitute for the intermediate stage phenol formaldehyde resin mentioned above is Silastic R.T.V. 501, a fluid silicone rubber which polymerizes within 2–6 hours at room temperature with the aid of a catalyst to a tough, tear resistant rubber.

The term "negative mold" as used herein means that the features manifested on the surface of the mold are in negative or reverse relief as compared to the features of the desired multicolor printing member and those of the positive or master mold from which the negative mold may be prepared in accordance with the method discussed in this example.

EXAMPLE 1

50 parts of polyvinyl chloride and 5 parts of tribasic lead sulfate, a stabilizer, were mixed with 50 parts of tricresyl phosphate to form a paste. To this paste was added 5 parts of methyl violet together with 100 parts of ethyl hexanediol serving as a vehicle therefor. Similar ink containing plastisols were prepared using calcazine red and neolan black as the coloring agents. These inks containing plastisols were poured into the separate cavities of the multicavity negative mold of Example A. A polyvinyl chloride film of approximately 10 mills in diameter was laid over the ink containing plastisols in the negative mold. The mold was then closed by placing an iron plate over the polyvinyl chloride sheet. The mold was then placed in an oven and heated to a temperature of about 350° F. for a period of 15 minutes. Thereafter the mold was removed from the oven, cooled, and the resultant multicolored printing member stripped from the mold. The printing member carried the photograph and surrounding printing characters in fine detail. There was no mingling of the colors during formation due to the fact that each separate color containing plastisol was maintained in its own cavity of the multicavity mold during formation. Further, there was no mingling of the colors after the formation of the printing member because the printing members were maintained in a noncontiguous relationship by the backing which had become an integral part of the printing member during the heating step. Glue was placed on the back of the printing member comprising principally the polyvinyl chloride sheet which had become fused to the microporous microreticulated resin formed by the ink containing plastisols. The printing member was then fixed to a conventional hand stamp stock. The printing member did not bleed at the backing when placed under pressure to exude ink from the pores of the printing and photographic indicia. It was used to make several thousand vivid imprints without reinking.

EXAMPLE 2

Example 1 was repeated with comparable results, the steps of the process being the same except that the multicavity negative mold containing the different colored ink containing plastisols was placed in an oven and heated to a temperature of approximately 250° F. for 8 minutes prior to the time the polyvinyl chloride backing was applied. After applying the backing, the mold was covered, replaced in the oven, and heated to a temperature of about 350° F. for an additional 10 minutes. As in Example 1, the final structure was a multicolor printing member consisting of a plurality of microporous microreticulated resin structures carrying ink of different colors, each being bonded in a noncontiguous relationship to an ink impervious thermoplastic backing.

EXAMPLE 3

Example 1 was repeated using in place of the thermoplastic film there specified, a fiber board which had been impregnated on one side with a polyvinyl chloride-polyvinyl acetate resin. The impregnated side of the fiber board was placed next to the plastisol. The printing member thus formed consisted of a microporous microreticulated resin bonded to a fiber board through an ink impervious plastic layer. Like the printing members of Examples 1 and 2, the multicolored inks contained in the multicolored printing member did not become comingled either during or after formation of the printing member.

EXAMPLE 4

Example 3 was repeated with comparable results by preheating the negative mold containing the plastisol containing ink as indicated by Example 2. The advantage of the preheating step is that it provides a more firm composition, the partially cured ink containing plastisol, to which to apply the backing.

EXAMPLE 5

Example 1 was repeated substituting a plastisol comprising equal parts of polyvinyl chloride resin powder of about 200 mesh size and tricresyl phosphate as a plasticizer therefor in place of the polyvinyl chloride sheet. The final structure was a multicolored printing member comprising a plurality of microporous microreticulated resin segments with the pores thereof filled with different colored inks bonded to an ink impervious backing formed by the coalesced ink-free plastisol. A multicolor printing member of this type can be seen in FIGURE 4. Microporous resin segments **29**, **30**, and **31**, each containing a different colored ink is bonded in a noncontiguous relationship to the ink impervious backing **32**.

EXAMPLE 6

Example 5 was repeated, except that the multicavity negative mold containing the ink containing plastisols was placed in an oven and heated to a temperature of approximately 200° F. for about 10 minutes prior to the time that the ink-free plastisol was poured over the negative mold. The mold was again placed in an oven and heated to a temperature of about 350° F. for 15 minutes. The preheating step had the advantage of solidifying or gelling the plastisols containing ink prior to the time that the ink-free plastisol was poured thereover. Thus, there was no diffusion of the ink in the plastisol containing ink into the plastisol comprising the backing as occurred to a limited degree in Example 5.

(*B*) *Preparation of Single Cavity Negative Mold*

A single cavity negative mold was prepared in a manner identical to that of Example A (Preparation of Multicavity Negative Mold) except that grooves **13** and **14** were omitted from the positive mold of FIGURE 1. The resulting negative mold was similar to that shown in FIGURE 2 except that it did not possess the dividing barriers **16** and **17**.

EXAMPLE 7

50 parts of polyvinyl chloride 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 100 parts of glycerol monoricinoleate, serving as a vehicle therefor. This ink containing plastisol was poured into a negative mold of Example B. A polyvinyl chloride film approximately 4 mills in thickness was laid over the ink containing plastisol in the negative mold. The mold was then closed by placing an iron plate over the top of the polyvinyl chloride sheet. The mold was placed in an oven and heated to a temperature of about 350° F. for a period of about 15 minutes. Thereafter the mold was removed from the oven, cooled, and the resultant printing member stripped from the mold. Glue was placed on the back of the printing member, comprising principally the polyvinyl chloride sheet which had become fused to the microporous microreticulated resin formed by the ink containing plastisol. The printing member was then fixed to a conventional hand stamp stock. In operation, the printing member made several thousand vivid prints. The printing member did not bleed at the backing when placed under pressure necessary to exude ink from the pores of the printing surface.

EXAMPLE 8

Example 7 was repeated with comparable results except that the negative mold filled with the ink containing plastisol was placed in an oven and heated to a temperature of approximately 200° F. for 10 minutes prior to the time the polyvinyl chloride backing was applied. After applying the backing, the mold was covered, replaced in the oven and heated to a temperature of about 350° F. for an additional 10 minutes. As in Example 7, the final structure was a printing member consisting of a microporous microreticulated resin bonded to an ink impervious thermoplastic backing.

EXAMPLE 9

Example 7 was repeated using in place of the thermoplastic film there specified, a fiber board which had been impregnated on one side with a polyvinyl chloride-polyvinyl acetate resin. The impregnated side of the fiber board was placed next to the plastisol. The printing member thus formed consisted of a microporous microreticulated resin bonded to a fiber board through an ink impervious plastic layer.

EXAMPLE 10

Example 9 was repeated with comparable results by preheating the negative mold containing the ink containing plastisol as indicated by Example 8. The advantage of the preheating step is that it provides a more firm composition, the partially cured ink containing plastisol, to which to apply the backing.

EXAMPLE 11

Example 7 was repeated, substituting a plastisol comprising equal parts of polyvinyl chloride resin powder of about 200 mesh size and dioctyl phthalate as a plasticizer therefor, in place of the polyvinyl chloride sheeting. The final structure was a printing member comprising a microporous microreticulated resin with the pores thereof filled with ink bonded to an ink impervious backing formed by the coalesced plastisol.

EXAMPLE 12

Example 11 was repeated except that the negative mold containing the ink containing plastisol was placed in an oven and heated to a temperature of approximately 200° F. for about 10 minutes prior to the time that the ink-free plastisol was poured over it. It was again placed in an oven and heated to a temperature of about 350° F. for 15 minutes. The preheating step had the advantage of solidifying or gelling the ink containing plastisol prior to the time the ink-free fluid plastisol was poured thereover. Thus, there was no diffusion of the ink in the ink containing plastisol into the plastisol comprising the backing as occurred to a limited degree in Example 11.

EXAMPLE 13

A mold similar to that shown in FIGURE 3 with barriers **22** and **23** removed was filled with the ink containing plastisol of Example 7 and heated to a temperature of 340° F. for 20 minutes to form a microporous microreticulated resin containing ink in the pores thereof. A type-cut stencil was cut and placed over the resin. A sheet of paper was pressed against this stencil and removed. The paper thus received a clear imprint of the type-cut upon the stencil, the ink having fed from the microporous resin through the stencil openings onto the paper.

EXAMPLE 14

The bottom of the three cavities of a mold similar to that shown in FIGURE 3 with barriers **22** and **23** removed was covered to a depth of about ⅛ of an inch with an ink-free plastisol consisting of equal parts of 200 mesh polyvinyl chloride and dioctyl phthalate. Barriers **22** and **23** were put in place so that their bottom edge was slightly submerged in the ink-free plastisol. Three different colored ink containing plastisols of the compositions disclosed in Example 1 were poured gently into the separate cavities of the mold covering the ink-free plastisol. The plastisols were covered with a metal plate and heated to a temperature of 350° F. for 20 minutes, cooled, and stripped from the mold. The molded structure consisted of three non-contiguous microporous microreticulated resins each containing a colored printing fluid of a color different from the other two bonded to a nonporous ink-free plastic backing. This multicolored molded resin was mounted on a cylindrical drum of a conventional mimeograph machine in place of the fibrous pad manually used. The nonporous portion of the resin was next to the drum, and the smooth face of the microporous portion of the resin was exposed. Over the three sections of the smooth face of the ink containing microporous resin there was fixed a type-cut stencil. The drum was rotated several hundred times, bringing clean sheets of paper into contact with the face of the resin. Each sheet received a clear imprint in three colors corresponding to the stencil type cuts.

The advantages of printing assemblies such as those disclosed in Examples 13 and 14 are manyfold. It is unnecessary to ink the pad, bringing many attending advantages. There is no ink leakage as there often is from the drum of the conventional mimeograph machine. Ink feed from the resin is more constant than from fibrous, felt or rubber pads normally used and fed by a viscous ink from the drum cavity. The drum or other device upon which the resin may be mounted may be left in any position without fear of leakage. Most conventional duplicating devices must be left in a position so that the ink will not flow from the ink well through the pad and stencil. The printing fluid is retained in the present microporous composition by cohesive forces due to the resins' system of extremely minute pores. The ink is emitted only when a porous article is brought in touch with it and upon the application of a slight pressure.

Now having generally described the invention, what is claimed is:

1. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises filling a plurality of cavities of a multicavity negative mold, each cavity separated from the others by a barrier and carrying the desired printing characters in negative relief, with an ink containing plastisol to a depth whereby the exposed surface of the plastisol is substantially level with the upper portions of said barriers, the plurality of cavities containing a plurality of colors when filled, heating said plastisol to a temperature sufficient to form a gel, superimposing over said plastisol an ink impervious thermoplastic film and heating said plastisol and film to produce a microporous microreticulated resin containing an ink in the pores thereof bonded to said thermoplastic film.

2. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises filling a plurality of cavities of a multicavity mold, each cavity separated from the other by a barrier and carrying the desired printing characters in negative relief, with a plastisol containing ink to a depth sufficient to cover the printing characters, but of insufficient depth to flow over the barriers separating the cavities, the plurality of cavities containing a plurality of colors when filled, heating said plastisol to a temperature sufficient to form a gel, placing an ink-free plastisol over an exposed portion of said gelled plastisol and heating said gelled plastisol and ink-free plastisol to produce a microporous microreticulated resin containing ink in the pores thereof bonded to an impervious layer of a coalesced resin.

3. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding segments of the mold which correspond to separate color areas of the desired printing member, forming a multicavity negative mold of the desired printing member having barriers bounding the cavities of the mold which correspond to separate color areas of the desired printing member by casting a thermosetting resin upon said positive mold, filling the cavities of said negative mold with an ink containing plastisol, the plurality of cavities containing a plurality of colors when filled, superimposing over an exposed portion of said plastisol an ink impervious thermoplastic film and heating said plastisol and film to produce a microporous microreticulated resin containing ink in the pores thereof bonded to said thermoplastic film.

4. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding the segments of the mold which correspond to the separate color areas of the desired printing member, forming a multicavity negative mold having barriers bounding the cavities of the mold which correspond to separate color areas of the desired printing member by casting a thermosetting resin upon said positive mold, filling the cavities of said negative mold with an ink containing plastisol, the plurality of cavities containing a plurality of colors when filled, superimposing over an exposed portion of said plastisol an ink impervious thermoplastic film bonded on one side to a fibrous sheet, the thermoplastic side being next to the plastisol, and heating said plastisol and film to produce a microporous microreticulated resin containing ink in the pores thereof bonded to said thermoplastic film.

5. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding the segments of the mold which correspond to the separate color areas of the desired printing member, forming a multicavity negative mold of the desired printing member having barriers bounding the cavities of the mold which correspond to separate color areas of the desired printing member by casting a thermosetting resin upon said positive mold, at last partially filling the cavities of said negative mold with an ink containing plastisol, the plurality of cavities containing a plurality of colors when filled, heating said ink containing plastisol to a temperature sufficient to form a gel, placing an ink-free plastisol over said gelled ink containing plastisol, and heating said gelled and ink-free plastisols to produce a microporous microreticulated resin containing ink in the pores thereof bonded to an impervious layer of coalesced resin.

6. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding segments of the mold which correspond to separate color areas of the desired printing member, forming a multicavity negative mold of the desired printing member having barriers bounding the cavities of the mold which correspond to separate color areas of the desired printing member by casting a thermoplastic resin upon said positive mold, filling the cavities of said negative mold with an ink containing plastisol, the plurality of cavities containing a plurality of colors when filled, superimposing over an exposed portion of said plastisol an ink impervious thermoplastic film and heating said plastisol and thermoplastic film to produce a microporous microreticulated resin containing ink in the pores thereof bonded to said thermoplastic film, the melting point of said thermoplastic resin from which said negative mold is formed being higher than the temperature at which said ink containing plastisol and said thermoplastic film are heated to produce the microporous microreticulated resin bonded to the thermoplastic film.

7. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding the segments of the mold which correspond to the separate color areas of the desired printing member, forming a multicavity negative mold having barriers bounding the cavities of the mold which correspond to separate color areas of the desired printing member by casting a thermoplastic resin upon said positive mold, filling the cavities of said negative mold with an ink containing plastisol, the plu-

rality of cavities containing a plurality of colors when filled, superimposing over an exposed portion of said plastisol an ink impervious thermoplastic film bonded on one side to a fibrous sheet, the thermoplastic side being next to the plastisol, and heating said plastisol and thermoplastic film to produce a microporous microreticulated resin containing ink in the pores thereof bonded to said thermoplastic film, the melting point of said thermoplastic resin from which said negative mold is formed being higher than the temperature at which said ink containing plastisol and said thermoplastic film are heated to produce the microporous microreticulated resin bonded to the thermoplastic film.

8. A method of making a printing member capable of producing a multicolored imprint in a single operation which comprises preparing a positive mold of the desired printing member having recess areas bounding the segments of the mold which correspond to the separate color areas of the desired printing member, forming a multicavity negative mold of the desired printing member having barriers bounding the cavities of the desired printing member by casting a thermoplastic resin upon said positive mold, at least partially filling the cavities of said negative mold with an ink containing plastisol, the plurality of cavities containing a plurality of colors when filled, heating said ink containing plastisol to a temperature sufficient to form a gel, placing an ink-free plastisol over said gelled ink containing plastisol, and heating said gelled and ink-free plastisols to produce a microporous microreticulated resin containing ink in the pores thereof bonded to an imperivous layer of coalesced resin, the melting point of said thermoplastic resin from which said negative mold is formed being higher than the temperature at which said ink containing plastisol and said ink-free plastisol are heated to gel the ink containing plastisol and to produce the microporous microreticulated resin bonded to the impervious layer of coalesced resin.

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