

Sept. 8, 1964

J. F. BRODERICK ETAL

3,147,705

FLEXIBLE PRINTING PLATES WITH IMPROVED PRINTING SURFACES

Filed Aug. 7, 1961

2 Sheets-Sheet 1

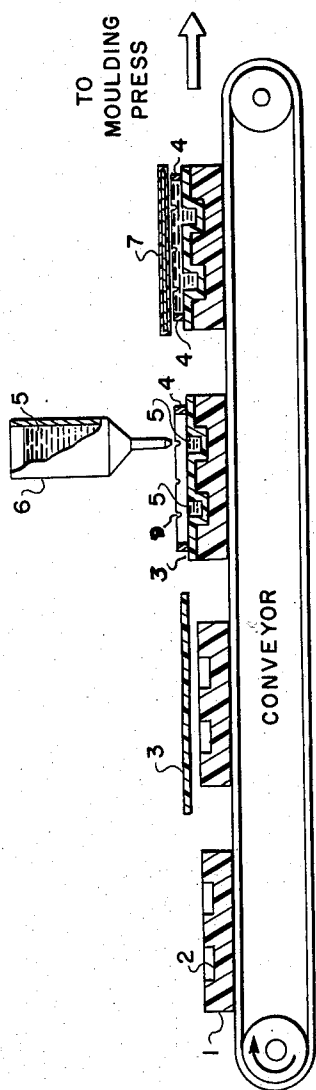


Fig. 1

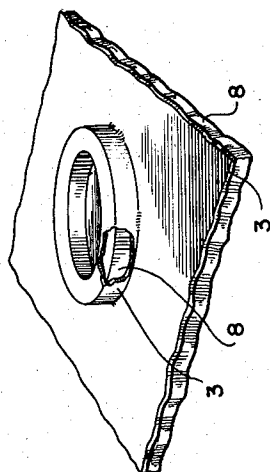


Fig. 2

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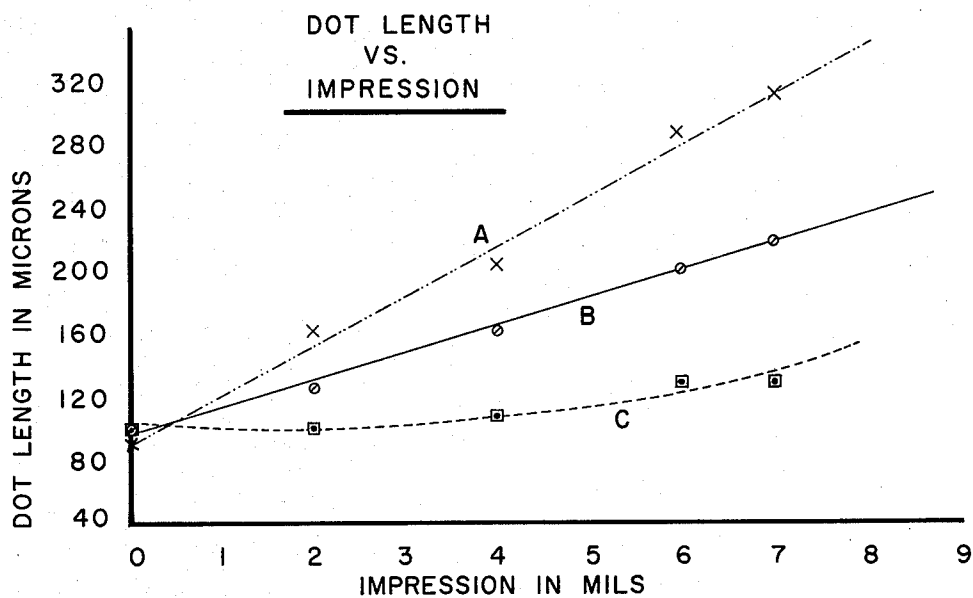
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2 Sheets-Sheet 2



LEGEND:

A = RUBBER

B = THERMOSET LIQUID POLYMER

C = THERMOSET LIQUID POLYMER WITH HARD FILM BONDED
TO PRINTING SURFACE

FIG. 3

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FLEXIBLE PRINTING PLATES WITH IMPROVED PRINTING SURFACES

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Filed Aug. 7, 1961, Ser. No. 129,820

6 Claims. (Cl. 101—379)

This invention relates to letterpress printing plates and, in particular, to plates suitable for use on rotary presses. In a specific aspect, it relates to flexible plates having a printing surface of increased hardness derived by firmly bonding a skin sheet of hard material thereto.

Rotary presses operate at speeds far beyond that permitted by the reciprocating motion of flat bed presses and are employed for all high-speed and large-scale printing operations, such as newspapers and national magazines. Of the major types of duplicate plates in such use, the electrotype represents the standard in dimensional stability, quality of reproduction, and durability. It is generally made flat and is curved by mechanical pressure for use on rotary presses. Preparation of electrotypes, however, is a slow process which consumes several hours in forming the matrix, electrodepositing a metal thereon, and finishing the resulting plate for mounting on the press. In addition, a large area of floor space, many pieces of heavy equipment, and a force of at least seven or eight skilled operators are required. Still further, several hours are devoted to make-ready on the press before printing can commence.

Rubber plates have gained extensive use in rotary press printing because of their flexible nature coupled with the fact that they can be made rapidly and economically. Ordinary plate rubber, however, is not a hard material. It usually has a hardness of about 50 to 60 (Shore A durometer), and this property has its advantages and disadvantages. On one hand, thickness tolerances for reasonably good quality printing are wider and make-ready on the press is minimized. On the other hand, the softness of the plates militates against their use where fineness of detail must accurately be reproduced, and they are normally considered unsatisfactory, for example, for reproducing halftone illustrations.

In the halftone process, a plate is obtained in which tonal pictures or continuous tone photographs are reproduced by a graduated system of spaced dots in relief. The number of dots which may appear on a plate ranges from about 65 to 150 per inch in both directions and they are usually of a size nearly invisible to the unaided eye. In view of the large number of dots, their minute size, and their close proximity to each other, it is imperative that the printing face of the plate be of sufficient hardness so as to withstand deformation of the dots when subjected to printing pressure. If the face of the plate is insufficiently hard, then the tips of the dots will be compressed closer to each other during the printing operation and consequently the image is not faithfully reproduced. In such case, the transferred image is spotted with blurred areas, thus destroying the original tonal values.

It is, therefore, an object of this invention to provide flexible printing plates suitable for use on rotary presses. It is another object to provide flexible plates which can be prepared as rapidly and economically as rubber plates but have a harder printing surface. It is a further object of this invention to provide plates which reproduce fine detail and halftone illustrations of a quality comparable to electrotypes.

These objectives are attained by providing a printing plate which includes a flexible body portion bearing relieved indicia on its face and a pellicle of hardened mate-

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rial firmly bonded to said face. The pellicle is derived from a thin, flexible film of a thermosoftenable material which, when bonded to the body portion, increases the hardness of the printing surface considerably without impairing appreciably the overall flexibility of the plate. The plate is formed by disposing the film over the cavity of a matrix, superimposing the body-forming material on the film, and subjecting the thus-assembled unit to molding conditions in a heated press. At elevated temperatures, the film is softened and compressed with the body-forming material into the incised areas of the matrix. When the molding cycle is completed, the softened film solidifies to a uniform, smooth, hard skin sheet which appears continuous with the printing face of the body portion to form an integral plate.

In the drawings:

FIGURE 1 is partly in section and illustrates successive steps which may be followed to prepare the duplicate plates of this invention.

FIGURE 2 illustrates a portion of a finished printing plate with the letter "O" being magnified and partially cut away to show the components of the plate.

FIGURE 3 is a graph which compares the quality of reproducing fine detail obtained from three different types of flexible printing plates.

In preparing the improved plates, a type form is first made by any typesetting process and complete with halftone etchings so mounted that their printing surfaces are level with the type faces. The lettering and illustrations on the form are raised in relief and in mirror reversal of the original. A matrix or mold is then made of the type form by depressing the relieved surface into a thermosetting material, such as a phenolic impregnated paperboard, at high temperature wherein a cavity is formed bearing the relieved images incised therein in positive form. The resulting matrix is then laid flat with the cavity side upward, and the surface of the cavity is sprayed with a release agent to facilitate separation of the plate from the matrix. A non-volatile fluid, such as one containing a silicone oil, has been found effective for this purpose.

A thin, flexible film of a thermosoftenable polymeric material is then disposed over the cavity of the matrix to provide increased hardness to the printing surface of the ultimate plate. Film thickness must be such that, on one hand, it is sufficiently thick to provide the plate with a desirable degree of surface hardness so as to effect a faithful transfer of halftone illustrations and, on the other hand, it must not be excessively thick so as to decrease the overall flexibility of the plate appreciably. Ordinarily, film thickness may range from about .0005 to .010 inch, preferably .001 to .005, to achieve the desired results.

To be effective, the film must be one which is hard and flexible at room temperature and softens but does not liquefy at molding temperature. By "soften" is meant that the film is capable of being deformed in any direction by the application of heat without rupturing. A thermosoftenable film can thus be worked during the molding step so as to completely envelop the tops and sides of the relieved printable indicia as well as coating the planar surfaces of the plate. When removed from the heated press, the softened film resolidifies in its deformed state to provide a smooth uniform coating to the plate printing surface which appears continuous therewith. A film which liquefies at molding temperatures is undesirable because the liquid will tend to localize in certain areas, leaving other areas uncoated, and thus giving a plate having a non-uniform coating on its printing surface.

The selected film must be compatible, that is, it must be capable of firmly bonding with the body portion of the plate so as to withstand peeling during prolonged printing runs. An obvious criterion is that it must also

be chemically resistant to inks and solvents normally used in printing.

Illustrative thermosettable films include polyvinyl chloride; vinyl chloride copolymerized with another polymerizable monomer, such as 3-15% vinyl acetate; polyamide resins (nylon); polyethylene terephthalate (Mylar); vinylidene chloride resins (Saran); vinylidene fluoride resins; chlorinated polyethylene; and polytrifluorochloroethylene (KEL-F). Homopolymers and copolymers of vinyl chloride are preferred because the body portion of the plate generally is prepared from like materials and, therefore, excellent adhesion of the film and body portion is assured. A substantially unplasticized film is preferred because maximum surface hardness can be obtained, while films containing large amounts of plasticizer not only impair the surface hardness but the plasticizer may be subject to extractability by inks and solvents during the printing operation. Although some plasticizer may be incorporated in the film during its manufacture to assist the extruding process, the amounts so used are of such small order that no deleterious effects have been experienced when films containing between about 0.25 to 1.0 percent plasticizer were applied to printing plates of this invention.

After the film has been placed over the cavity of the matrix, the material which forms the flexible body portion of the plate is then superimposed on the film. A number of materials can be used for this purpose including sheet materials, such as butadiene-acrylonitrile copolymers (Buna N plate gum); thermoplastic liquids, such as plastisols comprised of polyvinyl chloride dispersed in a suitable plasticizer; and liquid thermosettable compositions comprising a halogen-containing polymer and an imidazoline. With sheet material, fine detail is not easily reproduced due to the reluctance of such materials to fill the minute depressions of the matrix. Plastisols flow readily and penetrate the impressions in the matrix with ease, but they are thermoplastic and, therefore, the result-

Imidazolines are strong organic bases, highly reactive with many reagents, and many possess strong surface activity. In these compositions, their principal function is to crosslink the polymeric chains. The preferred imidazolines for use in this invention are those which in themselves are non-volatile and chemically stable at curing temperatures. In addition, they should be such that the uncured mixture with the halogen-containing polymer undergoes no change with time.

The imidazolines may be prepared by contacting appropriate amounts of polyamines and mono- and/or polycarboxylic acids at reactive temperatures and pressures. The temperature may range between about 150° C. and 240° C. and the operable pressure may range between about .1 mm. and 760 mm. Hg. Suitable polyamines are ethylene and propylene diamine, diethylene and dipropylene triamine, triethylene tetramine, and tetraethylene pentamine. Suitable monocarboxylic acids are those containing from 1 to 18 carbon atoms, or even more, such as acetic, caproic, pelargonic, lauric, palmitic, oleic, and stearic acids; suitable polycarboxylic acids include those having from 3 to 36 carbon atoms, such as adipic, pimelic, suberic, azelaic, sebacic, and dimerized and mixtures of dimerized and trimerized fatty acids. In addition, mixtures of mono- and/or polycarboxylic acids may be used. It is, of course, within the scope of this invention to use polyimidazolines, i.e., compounds having more than one imidazoline ring. These may be prepared by reacting mono- and polycarboxylic acids or mixtures thereof with a polyamine having more than two amino groups, such as triethylene tetramine, or mixtures of polyamines.

The following table illustrates reactants and reaction conditions which may be employed to prepare a representative number of imidazolines and polyimidazolines for use in forming the body portion of the plate. Various combinations of acid and amine may be employed and this table should be considered as representative and not exhaustive of the many possible combinations:

TABLE

Product	Acid	Moles	Amine	Moles	Reaction Conditions		
					Pressure, mm. Hg	Temp., ° C.	Hours
A-----	Sebacic-----	1	Triethylene tetramine.	2	760-15	150-220	4
B-----	Oleic-----	1	do-----	6	760-15	150-200	4
C-----	Sebacic-----	5	do-----	2	760-15	150-220	4
D-----	Oleic-----	2	do-----	1	760-15	150-200	4
E-----	Sebacic-----	1	do-----	1	760-50	150-200	4
F-----	Acetic-----	1	Diethylene triamine.	1	760-20	150-220	4
G-----	Pelargonic-----	1	do-----	8	760-20	150-220	4
	Empol 1022 ¹ -----	1	Triethylene tetramine.	2			
	Oleic-----	4	do-----	1			
	Sebacic-----	3	do-----	1			
	Empol 1024 ¹ -----	1	do-----	1			

¹ Mixtures of polymerized acids comprising about 75 percent dimeric and 25 percent trimeric acids derived from a mixture of unsaturated 18-carbon monocarboxylic fatty acids.

ing plates must be cooled before they can be separated from the matrix. Another objection to the use of plastisols is that the plasticizer content is only physically mixed with the resin and may migrate into the film, thereby reducing the surface hardness of the plate.

The preferred materials for forming the body portion are the liquid thermosettable compositions. Such materials readily penetrate all impressions in the matrix, and because of their infusible nature the resulting plates may be separated from the matrix while hot without causing distortion. Accordingly, the invention will be further described with respect to the use of the liquid thermosettable compositions comprising the halogen-containing polymer and an imidazoline as the preferred materials in preparing the body portion of the plate, although it is to be understood that the other materials specified above provide improved plates subject to the limitations indicated.

The imidazoline is first pre-reacted with an epoxy compound before it is mixed with the halogen-containing polymer to provide the resulting printing plate with the desirable degree of flexibility. When the composition is cured during the molding step, the epoxy compound is chemically grafted to the halogen-containing polymer through the imidazoline, thus rendering it inextractable by inks and solvents. Suitable epoxy compounds include epoxidized triglycerides of vegetable oil fatty acids, such as epoxidized soybean oil and epoxidized castor oil, and epoxidized esters of lower alkyl alcohols and unsaturated fatty acids. Representative compounds of the latter group include methyl-, ethyl-, propyl-, and butyl-9,10-epoxystearate; butyl-9,10,12,13-diepoxystearate; butyl-9,10-epoxypalmitate; and butyl-12-hydroxy-9,10-epoxystearate. Reaction of the imidazoline and the epoxy compound proceeds quite readily when carried out at temperatures between about 100° C. and 190° C., and preferably be-

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tween about 130° C. and 150° C. The constitution of the imidazoline-epoxy compound reaction product may vary and is dependent upon the particular reactants used consistent with the degree of flexibility which is desired in the printing plate.

In making the liquid thermosettable print plate composition, the halogen-containing polymer is thoroughly dispersed in the pre-reacted imidazoline-epoxy compound fluid product. The mixture is stable at room temperature and the pre-reacted fluid reacts with the polymer only after heating. Thus, no polymerization or crosslinking takes place until the composition is heated in the press at about 120° C. to 200° C. for about 1 to 12 minutes and preferably at about 150° C. to 165° C. Upon heating to the softening point of the dispersed polymer, a reaction sets in which leads to chemical crosslinking of the polymer and chemical attachment of both imidazoline and epoxy molecules thereto. The result is a highly adhesive, non-thermoplastic polymer which binds well with polyvinyl chloride films.

Preparation of a specific imidazoline-epoxy compound reaction fluid is illustrated in Example I.

Example I

67.7 pounds (.24 mole) of oleic acid and 36 pounds (.06 mole) of "Empol 1024" were mixed together in a glass vacuum vessel and then 36.4 pounds (.18 mole) of sebacic acid were added. The acids were heated to about 70° C. and then 70.2 pounds (.48 mole) of triethylamine tetramine were added. 0.21 pound of powdered sodium tripolyphosphate was then added to inactivate and chelate any metal impurities which may be present in the acids and amine. The reactants were vigorously agitated and a nitrogen atmosphere was applied and maintained throughout the reaction period. The mixture was heated initially at one atmosphere to about 150° C. and the temperature was gradually raised until a value of about 220° C. was reached over a three-hour period while the pressure was correspondingly reduced from 760 to 20 mm. Hg. The reaction was then continued for one hour at 220° C. and 20 mm. Hg. Water of condensation was removed throughout the reaction period as formed. The amount of water removed corresponded with about 85 percent conversion of the carboxyls to imidazoline groups, leaving a balance of the carboxyls in the form of amides as confirmed by infrared absorption analysis. The product was then cooled to 130° C. Three hundred pounds of epoxidized soybean oil were heated to 130° C. in an open vessel and then 100 pounds of the foregoing imidazoline product (already at a temperature of 130° C.) were added slowly with stirring. When all of the imidazoline was added, the mixture was reacted at 130° C. for about one hour with gentle stirring and then cooled. The reaction proceeded smoothly and gave a product which was permanently fluid at room temperature. Care was taken to protect the reaction mixture and the cooled product from moist air and/or carbon dioxide, each of which tends to produce bubbles in the final print plate.

While the imidazoline is a highly effective curing agent for halogen-containing polymers, such as polyvinyl chloride and copolymers of vinyl chloride, its curing action must be controlled to avoid degradation of the polymer when the composition is heated in the press. To regulate the curing action of the imidazoline, a metallic compound, such as zinc oxide, is added to the composition. The zinc oxide retards blackening on heating, prevents gas evolution and augments resistance to moisture while retaining the advantage of imidazoline cure. The grade of zinc oxide is not a critical factor so long as good dispersion is obtained. A particle size of about .5 micron is quite effective.

An agent is also added to sequester any moisture which may remain in the composition after it is manufactured or which may reach the composition accidentally during storage and/or use. The presence of moisture is undesir-

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able because it forms bubbles in the molded plate which adversely affect its printing surface. Any material which would form a compound with water at room temperature and which, when combined with the water, would not decompose at about 175° C. would be a suitable moisture-sequestering agent provided it could be reduced to a finely divided state so as to obtain good dispersion and would not cause any undesirable side effects. Quicklime, Portland cement, and barium oxide have been satisfactorily used for this purpose. White Portland cement is preferred because it disperses readily to provide a more homogeneous plate.

The imidazoline-epoxy compound reaction product, zinc oxide and the moisture-sequestering agent form a composition which is quite viscous and a satisfactory plate can be made using only these ingredients. However, its viscous nature makes handling and workability of the composition difficult. To alleviate these difficulties, a viscosity-lowering agent is included in the composition. Suitable agents include polyethylene glycol stearate, condensation products of ethylene oxide and propylene glycol, sorbitan monopalmitate, sorbitan monooleate, 3,5-dimethyl-1-hexyn-3-ol, and the fatty acid esters of polyethylene glycol 200-600 series (the designation numbers indicate the approximate molecular weight of the polymeric glycol minus the weight of the fatty acid moiety). Polyethylene glycol 400 monooleate is quite effective for this purpose.

The composition may be prepared by charging the requisite amounts of all ingredients in a single pass to a suitable mixing apparatus, or by adding the ingredients incrementally. Whatever method is selected, mixing is carried out until all ingredients are thoroughly and uniformly dispersed to form a homogeneous liquid. A preferred method of carrying out the mixing operation is to first form a masterbatch to assure intimate dispersion of all ingredients and then gradually add the remaining portions of the formulation to the masterbatch. A typical masterbatch comprises zinc oxide, the moisture-sequestering agent, and a portion of the imidazoline-epoxy compound reaction product, the total of which amounts to about 3 percent of the final weight of the composition. The ingredients may be processed in a suitable homogenizer, or a pebble mill when large batches are prepared. After a prescribed preliminary mixing period, the masterbatch is withdrawn and, to complete its mixing cycle, it is passed to a mixing kettle in which a low pressure of about 25 mm. Hg or less can be reached and maintained. Constitution of a representative masterbatch is illustrated in Example II.

Example II

Ingredient:	Pounds
Imidazoline-epoxy compound reaction product of Example I	50
Zinc oxide	15
White portland cement	50

A complete formulation of the composition which is suitable for use as the body portion of the improved plates of this invention is shown in Example III. When cured, this composition gives a plate having a hardness value of about 95, Shore A durometer.

Example III

Ingredient:	Pounds
Polyvinyl chloride, paste grade	1615
Polyethylene glycol 400 monooleate	75
Imidazoline-epoxy compound reaction product of Example I	1012
Masterbatch of Example II	85

In preparing the composition of Example III, the entire amount of the imidazoline-epoxy compound reaction product is charged to a vacuum mixer and then the masterbatch is added with agitation. The components are mixed for a prescribed period, agitation is stopped, a portion of the polyvinyl chloride is then added, and the

mixer is closed and a vacuum applied. Agitation is resumed and continued until the polyvinyl chloride is thoroughly incorporated in the liquid. Agitation is again halted, the vacuum is released, and the step of adding the polyvinyl chloride incrementally is continued until the entire amount required by the formulation has been charged and thoroughly blended. Agitation under vacuum is then resumed and continued until all specks and lumps have been completely dispersed. Finally, the viscosity-lowering agent is added and stirred in under vacuum. Upon completion of the last step, the resulting liquid composition is ready for immediate use in molding the plates or it can be stored for subsequent use. Plate molding can be carried out by using the composition in liquid form, which is preferred, or the liquid may be partially processed by heating for a time sufficient only to form a solid sheet having a minimum amount of cure.

Preparation of the improved plates of this invention is illustrated in Examples IV to VI.

Example IV

A rigid matrix 1, prepared from a thermoset material, was provided bearing a cavity 2 in which the reproducible matter consisting of lettering and halftone illustrations was impressed. The halftones were produced from a 120-line screen plate. The matrix was laid flat with the cavity side upward and the surface of the cavity was sprayed with a layer of a non-volatile release fluid containing a silicone oil to assist subsequent separation of the plate from the matrix. A sheet 3 of polyvinyl chloride, .003 inch thick and containing 0.5% plasticizer, was then disposed over the cavity. (The sheet material was a commercial product known as Flex-O-Film Vinyl VR 611.) A frame 4, referred to as a restrictor chase, was then placed on the peripheral edge of the matrix to contain the liquid composition in the cavity. The chase is provided with a plurality of spaced milled gates 9 through which excess composition can escape during the molding operation.

When the chase had been properly placed, a portion of the liquid composition 5 of Example III was poured from a source 6 on top of the polyvinyl chloride sheet in amount sufficient to fill the cavity of the matrix. The entire assembly was then heated in an open press at a temperature of about 160° C. for approximately three to five minutes. The preheating period raises the temperature and lowers the viscosity of the liquid to a point where it flows readily in the mold and thus reaches the most difficultly accessible recesses therein and allows any bubbles of air, which may have been trapped during pouring, to escape. Following the preheating period, the entire assembly was covered with a Teflon-coated aluminum plate 7 and returned to the molding press. The press was then slowly closed in order to allow any air bubbles accidentally included therein to escape, and the pressure was raised to about 500 pounds per square inch over the chase area. The temperature was maintained at a steady level of 160° C. during the molding cycle. The assembly was kept in the press for nine minutes and then removed and disassembled. The resulting plate was immediately stripped from the matrix while hot without any damage to the plate or its printing surface.

An examination of the finished plate (FIGURE 2) revealed that the sheet of polyvinyl chloride film 3 adhered tenaciously to the printing surface, shown generally by the letter "O" giving it a glossy and smooth finish. (The numeral 8 refers to the solidified form of the liquid composition 5.) Measurements of adhesion of the film to the plate showed that it was about 35 ± 5 pounds per linear inch. When rubbed with the fingernail, the filmed plate gave a harsh, rattle-like sound while the unfiled plate gave a softer muffled effect. The differences in reproducing fine detail between a filmed and unfiled plate are shown in FIGURE 3 of the drawing. It is noted that the filmed plate gave a lower rate of dot size increase with increased impression than the un-

filed plate, indicating that more faithful reproduction is obtained by using the plate having the modified printing surface.

Similar plates were made from the liquid composition of Example III and according to the plate-molding technique of Example IV in which the sheet of polyvinyl chloride was substituted by a .004 inch thick film of polycarbonate and a .0005 inch thick film of polyvinylidene fluoride. Both films adhered well and gave plates having improved ability to reproduce fine detail over the unmodified plates.

Example V

A vinyl plastisol was prepared by stirring the following ingredients under vacuum in a mixing apparatus:

	Parts by weight
Polyvinyl chloride, paste grade	100
Dioctyl phthalate	20
Harshaw stabilizer 12-V-5 (bariumcadmium coprecipitated laurate)	3
Harshaw 7-V-2 (epoxy stabilizer)	3
Polyethylene glycol 400 monooleate	1

The resulting plastisol was very light-colored, extremely thixotropic, and did not flow easily and uniformly. A printing plate was made in a manner similar to the procedure of Example IV by superimposing the polyvinyl chloride sheet material of Example IV over the cavity side of a heated matrix and then pouring the plastisol over the sheet. The assembly was then heated in a press for nine minutes as described in Example IV, the preheating period being omitted. Following the press molding step, the assembly was cooled under pressure for five minutes, and the plate was then separated from the matrix. Upon examination, the resulting plate was found to exhibit a harder printing surface than a similar plate made without the polyvinyl chloride sheet but was not as hard as the plate made according to Example IV using the composition of Example III. This was believed to be due to migration of some plasticizer from the plastisol to the polyvinyl chloride sheet. Adhesion of the sheet to the plastisol body portion was very good, being slightly better than that obtained by the plate of Example IV. A comparison of printed matter produced from plates using the plastisol per se and plates prepared according to this example revealed the latter to give reproductions of improved clarity over the former.

Example VI

A strip of polyvinyl chloride sheet material as described in Example IV was disposed over a matrix and then a .105 inch thick sheet of solid Buna N plate gum was superimposed thereover. The plate gum was a compounded copolymer of butadiene and acrylonitrile distributed commercially by Williamson and Co. as N 50 B. Its use as a solid sheet eliminated the need of a chase. The assembled unit was placed in a heated press which was provided with bearers on each side of the unit to regulate the distance between the upper and lower press platens and consequently regulating the ultimate thickness of the resulting printing plate. The plate gum was cured in the press in eight minutes at 163° C. A cooling period was unnecessary. The polyvinyl chloride sheet exhibited excellent adhesion to the cured plate gum and gave a satisfactory hard printing surface. The rounding of corners on the type characters, however, was somewhat more pronounced than the plates of Example IV.

In order to obtain a comparison of the quality of reproduction of fine detail available from different types of flexible plates, the manner in which halftone dot size and shape varied with impression was investigated for three such plates. The plates investigated were: (A) A rubber plate having a hardness of 70 Shore A; (B) A plate molded from the thermosetting liquid composition of Example III; and (C) A plate molded according to Example

IV in which a sheet of polyvinyl chloride, .003 inch thick, was molded to the printing surface. Each plate was made on a matrix bearing suitable light shade halftone areas. The original from which the matrix was made had a depth of etch of .002 inch. Plates were molded about .115 inch thick and finished to .110 inch, $\pm .001$ inch, by grinding the back side with a Harley grinder.

Each plate was proofed several times on coated paper using a Vandercook proof press in which the impression was increased by a measured amount between successive proofs. The resulting proofs were then masked so as to expose the same small light shade halftone area on each and these areas were examined with a microscope equipped with a measuring eyepiece. The dots tended to elongate in the rotative direction of the printing cylinder and the length of dots were measured in microns. Since there was some variation between individual dots within the selected area, five were measured in each case and the results were averaged. Plots were made showing the manner in which dot length varied with degree of impression for each of the three plates. It was expected that the plate showing the lowest rate of increase of dot size with increasing impression would give the best reproduction of light halftone shades.

The results of the measurements are reflected in FIGURE 3 of the drawing. It will be noted that the rubber plate showed the greatest rate of increase in dot length with increasing impression while the thermosetting liquid material having the modified hardened printing surface showed the lowest rate of increase. As expected, the thermosetting liquid without the addition of the polyvinyl chloride to its printing surface gave an intermediate rate of increase between that of the rubber and that of the surface hardened plate.

Tests on commercial equipment gave results entirely in harmony with the results described above. The plates of this invention have a number of advantages over existing duplicate letterpress plates. They give a combination of mold fidelity, flexibility and hardness which is unobtainable by known flexible plates. By modifying the printing surface with a skin sheet of hard plastic material, reproduction is improved and the practical printing of halftones from flexible plates is now possible.

We claim:

1. A permanently flexible letterpress printing plate comprising a flexible thermoset polymeric body portion bearing relieved indicia on its face, said body portion com-

prising a halogen-containing polymer and the product derived by reacting an epoxidized ester and an imidazoline, and a skin sheet of flexible polyvinyl chloride firmly bonded to said face, said skin sheet appearing continuous with the printing face of the body portion.

2. A printing plate according to claim 1 wherein the halogen-containing polymer is polyvinyl chloride and the epoxidized ester is a member selected from the group consisting of epoxidized triglycerides of vegetable oil fatty acids and epoxidized esters of lower alkyl alcohols and unsaturated fatty acids.

3. A printing plate according to claim 2 wherein the epoxidized ester is epoxidized soybean oil.

4. A method for preparing a permanently flexible letterpress printing plate having a printing surface of improved hardness which comprises providing a cavernous image-bearing matrix, disposing a skin sheet of flexible polyvinyl chloride over the cavity of said matrix, superimposing a layer of a thermosetting polymeric material over the skin sheet, said polymeric material comprising a halogen-containing polymer and the product derived by reacting an epoxidized ester and an imidazoline, and heat-pressing the thus-assembled unit at a curing temperature, said thermosetting polymer being flexible in its thermoset state.

5. A method according to claim 4 wherein the halogen-containing polymer is polyvinyl chloride and the epoxidized ester is a member selected from the group consisting of epoxidized triglycerides of vegetable oil fatty acids and epoxidized esters of lower alkyl alcohols and unsaturated fatty acids.

6. A method according to claim 5 wherein the epoxidized ester is epoxidized soybean oil.

References Cited in the file of this patent

UNITED STATES PATENTS

1,377,509	Novotny	May 10, 1921
1,379,430	Yeoell	May 24, 1921
2,028,712	Swan et al.	Jan. 21, 1936
2,078,535	Hagedorn et al.	Apr. 27, 1937
2,558,269	Reilly	June 26, 1951
2,741,297	Vamvaketis	Apr. 10, 1956
2,875,051	DeMaria	Feb. 24, 1959

FOREIGN PATENTS

519,182	Canada	Dec. 6, 1955
713,990	Great Britain	Aug. 18, 1954