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RAISED PRINTING

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This invention relates to a method for making raised printing articles, and also relates to such raised printed articles. In particular, the invention relates to a method and product whereby thermosetting resins are deposited on surfaces of paper sheets in the form of intelligible or esthetic characters which are cured into raised, hardened and tough character impressions.

Raised printing is a desired practice in the art because of its attractiveness when used on letterheads, business cards, holiday greeting cards, and the like. The conventionally engraved printing is recognized as an expensive procedure and, accordingly, efforts have been made to provide raised printing more economically. One of such ways is the well known Virkotype method where rosin powders are sprinkled onto heavily printed ink characters and then heat dried. This attractive and successful printing process has limitations in that raised type is not thermally stable and, accordingly, the reverse side of the paper cannot be run through the same heat drying step. For some applications the adherence of this raised printing to the paper is not as strong as some practitioners may require. Printing on the reverse sides of the paper, and raised printing characters with extremely strong adherence to the paper, are highly desirable properties for braille printing. Placing greater amounts of information on a single sheet of paper will considerably reduce the bulk of matters transcribed into braille and, also, tthe strong adherence of the raised printing will permit such braille printing to be repeatedly read without effacing the braille characters.

It will be understood that the foregoing properties are also desirable for applying raised printing to reverse sides of greeting and holiday cards. Tough, hard raised printing will permit such cards to be freely handled without incurring chipping or other defacing of the raised printed characters.

It is accordingly a primary object of this invention to provide a method and product whereby raised printing may be simply and economically applied in a wide variety of ways to different types of paper, and on both sides of a single sheet of paper, if desired.

Another object is a method and product in which a raised printing is attractively and effectively provided in a serviceable manner so that said raised printing is securely adhered to the paper throughout extended use over long periods of time.

Another object is a method and product in which raised, intelligible or esthetic characters can be applied to the surface of paper in a color to satisfy various esthetic desires.

Another object is a method and product in which raised printing is provided on the surface of the paper in a way which permits the practitioner to control the height of the raised printing character.

Another object is a method whereby a thermosetting resin ink is printed on a sheet of paper in a raised form by utilizing economical and simple stencil plate methods.

Another object is a method for applying raised resin characters to the surface of a sheet of paper by forcing a resin mixture through a wide variety of stencils or simulated silk screens.

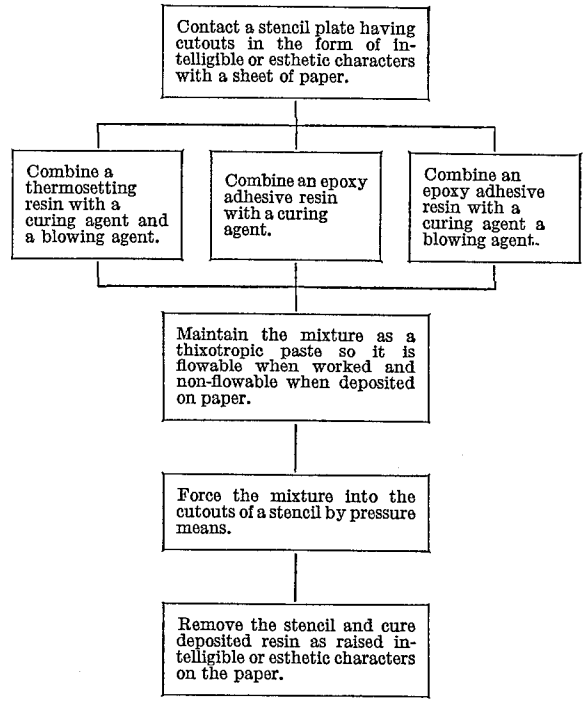
Another object is a method in which thermosetting

resin compositions are applied onto a surface sheet of paper so that the height of the thermosetting resin character is controlled.

Another object is a method in which epoxy resins are applied as raised printed characters on the surface of a sheet of paper to provide extremely strong bonding between the resin and the paper for repeated use over extended periods of time.

Another object is a product in which paper in the form of sheets, pages, cards or the like has raised and cured resin characters applied in an attractive manner with uniform color, if desired, to present an attractive, intelligible or esthetic pattern.

The foregoing objects are attained together with other objects which will become apparent from the present invention, the process whereby may be generally indicated by the following flow diagram:



Various thermosetting resins can be used to attain good quality raised printing because such resins are permanently set, that is, they are infusible to subsequent heat application. Such thermosetting resins are known to be hard and tough in their cured state which makes them desirable for many severe uses over extended periods of time. Representative resins which are useful are the polyesters, the phenolics, the polyurethanes and the epoxies. It has been found that the epoxy resin has marked advantages for the raised printing process because of its great bonding power which allows it to become securely adhered to the sheet of paper, and because it can resist spreading to thereby form a good quality, raised character.

The preferred epoxy resins are applied by forcing a resin mixture through cutouts or openings in any convenient stencil plate onto a sheet of paper placed in contact with such plate. The epoxy resins are the well known reaction products of epichlorohydrin and bis-phenol-A, and such resins are cured by combining them with well known curing agents. A heat cure can be optionally used to cure the resins after they have been deposited on the paper so long as the heat intensity is maintained below the char or scorch levels of the paper. It is required that the epoxy resin and curing agent mixture be a thixotropic

paste so that it is flowable when handled but becomes nonflowable when it is deposited as a raised character on the surface of the paper. Epoxy systems are available as a thixotropic paste, for example, the A–31 formulation supplied by the Armstrong Products Company. Such paste or pastes are easily provided as a two container system in which the resin and the curing agent are kept separate prior to actual mixing. The thixotropic paste consistency can be, however, maintained according to well known skills in the art by incorporating appropriate fillers. The flowability of the epoxy resin will depend on its molecular weight range which differs with the various types of resins which are available in numerous quantities. This flowability is controllable by the addition of fillers such as mica, aluminum oxide, talc, aluminium powder, short asbestos fibers, zinc duct and the like.

The epoxy adhesives additionally make improved raised characters because there is very slight shrinkage in the curing of such resins. The epoxy resins may be cured with the various primary, secondary or tertiary amines according to well known practices either at room temperature, with heat curing, or with both. Room temperature curing adhesives generally have curing agents which are cross-linking aliphatic amines such as diethyleneamine, triethyleneamine, diethylaminopropylamine, and catalytic amines such as tridimethylaminomethyl phenol. An epoxy system may be used which has latent curing agents, that is, an agent which reactive groups such as nitrogen which are blocked at ambient temperature conditions. Such blockage is removed by heat and the cure is initiated. Among such latent curing agents are amine salts, monoethylamine and triethanolamine borate.

Curing of epoxy resins is characterized by conversion of the epoxy groups and cross-linking. The greater the conversion and cross-linking, the more complete is the cure. In general, irrespective of the curing agent used, heat curing at temperatures higher than ambient will produce systems more thoroughly cross-linked and containing fewer unreacted or unconverted groups. It is accordingly provided as a preferred practice that the raised epoxy resin characters on the paper are heat cured.

The epoxy resin system is outstanding because of its firm bond to the paper, its toughness and the ability to lay the resin down on the paper without undue spreading on the paper or wetting the paper. This results in excellent quality characters which are well defined, precise and attractive. It has been found, however, that other thermosetting resins are advantageously used to apply raised printing when such resins are combined with a blowing agent to control the rise or height of the printed character on the paper. The amount of the blowing agent placed in the resin will control the rise and such amount will be readily determined by the skilled practitioner in accordance with the type of raised printed character he desires. It is, of course, required that such thermosetting resin mixtures, which include the resin and its curing agent, are also provided as a thixotropic paste so that it can be applied to the paper in the same way which was described in relation to the epoxy resins. In general, it has been found that there is an optimum concentration of blowing agent which may be incorporated to attain attractive raised printing. This is generally between 1 and 2% based on the weight of the resin mixture of resin and curing agent. Adding additional blowing agent will not significantly raise the printed characters and will disadvantageously impart voids which will tend to make the raised character brittle and removable. Of course, extremely small concentrations of blowing agent, substantially below 1%, will not result in the desired raising of the resin characters.

Without a blowing agent the height of the resin character is limited by the depth of the opening in the stencil plate, which usually coincides with the thickness of the stencil plate. The height of the printed character may actually be less than the depth of the plate when some spreading or wetting of the paper occurs. Inclusion of the blowing agent will provide that the height of the character is at least as high as the depth of the cutout in the stencil and may be selectively greater. Various blowing agents are known and available, and among them may be recited hydrocarbon solvents which function as blowing agents in resin compositions, azo-bis-nitriles, such as Azo-Cel 508, supplied by the Fairmont Chemical Company of Newark, N.J. and Kemcel K 9082 chemical paste supplied by the Claremont Polychemical Corporation, and the like.

Some of the representative blowing agents which may be used are listed in the following table by their commercial names and suppliers. The agents are believed to operate by evolving a gas such as nitrogen with the exception of Isopar M which is isoparaffin but which still operates as a blowing agent.

TABLE 1

Blowing agent:	Supplier
Isopar M	Humble Oil Co.
Kemcel K–9082	Claremont Polychemical Corp.
D–800	Lucidol Div., Wallace & Tiernan Inc.
Azo-Cel 50%	Fairmont Chemical Co., Newark, N.J.

It will be realized that the foregoing resin formulations may be modified in many ways and still remain within the confines of the present inventive concept. Thus, a thermosetting resin may be used essentially alone, or may be combined with other thermosetting resins or even portions of thermoplastic resins. It will be only necessary that the cured product has the characteristic of the thermosetting resin in that it is tough, hard, thermally stable and securely adhered to the paper. Some of the resin may be in essentially solid form, and, accordingly, appropriate amounts of solvents such as xylene or diethylene glycol monomethyl ether (Methyl Carbitol) may be used. When a blowing agent is incorporated in a thermosetting resin mixture, it may be desired to lower the decomposition temperature of the blowing agent, and this may be done by adding small amounts of appropriate lead compounds such as Dutch Boy Dyphos, supplied by the National Lead Company.

The polyester resins are appropriately cured by recognized catalysts such as benzoyl peroxide, cumene hydroperoxide and the like. In the polyester resin system, it is well known that low temperature and high temperature catalysts may be combined to initiate the curing action at lower temperature and to sustain it at higher temperatures. The rate of polyester curing can be controlled by the addition of other known ingredients such as cobalt naphthanate.

The polyurethane or isocyanate resins are combined with a recognized curing agent, and in the presence of atmospheric moisture undergo a foaming cure. A blowing agent may be omitted with the polyurethanes because of the inherent foaming property of this resin which will lead to a raised printed character. The degree of foam and the rate of cure is, of course, controlled by the amount of water and the type and amount of curing agent, all of which may be manipulated according to recognized practice.

The urethane resins are reaction products of polyisocyanate and a polyol such as polyglycol. The well known curing agents for the polyurethanes are the amines and glycols which may be used in various amounts to control the rate of curing and the characteristics of the cured product. Among the amines may be mentioned methylbis-chloroaniline, triethylene diamine, n-alkyl morpholine, dichlorobenzidine and others.

Phenolic resins may be used with a well known alkaline catalyst to immediately initiate curing towards the

thermosetting state. In a similar manner, urea formaldehydes may be employed.

Reference may be made to the following table for a list of representative resins which may be used, such references are identified by their commercial names and their supplier.

TABLE 2

Resins	Type	Supplier
Uralane 1723-6	Urethane	Furane Plastics Corp.
EPON 812	Epoxy	Shell Chemical Corp.
Adhesive A031	do	Armstrong Products Co., Inc.
Dow DER 667	Epoxy (Solid)	Dow Chemical Co.
Koplac 1580-5	Polyester	Koppers Co.
Koplac D3000-1500	do	Do.
Plenco 677	Phenolic	Plastics Engr. Co.
Resin ST 5085-2A	Phenolic (solid)	Schenectady Chemicals Inc.

The following Tables 3 and 4 represent a list of representative solvents some of which are identified by their commercial name and supplier, and a representative list of catalysts and curing agents, some of them being identified by the commercial names and suppliers.

TABLE 3

Solvents:	Supplier
Acetone	
Methanol	
Methyl Carbitol	
Xylene	
Triton X-100	Rohm and Haas Co.

TABLE 4

Catalysts and curing agents:	Supplier
Genamid 250	
Benzoyl peroxide	
Cumene hydroperoxide	
Hexamethylenetetramine	
Lupersol 11 (t-butylperoxy pivalat, 75% in mineral spirits)	Wallace & Tiernan, Inc.

The various compositions formulated for the practice of the invention may include other materials such as mixed monomers, clays, silica and carbon black. Some of these representative materials are listed in the following Table 5. Many of these are identified by commercial names and suppliers as listed.

TABLE 5

Materials:	Supplier
2-ethylhexyl acrylate	
Gelva emulsion, TS-100	Shawinigan Resins Corp.
Huber HT clay	Huber Clay Co.
Statex, carbon black powder	Columbia Carbon Co.
Cab-O-Sil M-5, silica	Godfrey L. Cabot, Inc.
Dutch Box Dyphos	National Lead Co.

The color of the raised resin printing can be controlled by incorporating into the resin mixture small amounts of a desired colorant such as colored powder, or carbon in the event black raised printing is desired. Colored powders such as bronze, silver, gold and ultra-marine may be added to the resin mixtures in amounts which will attain the desired depth of color. As a colorant, various pigments may be ground and dispersed in the resin or added as a color paste of a ground pigment in a non-volatile vehicle. Such pigments may include the red beta-oxy-naphthoic acid derivatives, the orange lead chromate lead molybdate, the green copper phthalocyanine chlorinated, the blue copper phthalocyanine and the like.

The resin mixture in the form of a thixotropic paste is forced through the cutouts or openings in a stencil plate which cutouts conform to a desired intelligible character such as block letter or script writing, dots for braille use, or esthetically pleasing designs which may be linear, planar or curvilinear. The dimensions of the cutouts may vary and it has been found useful to use cutouts with dimensions varying from one to three mm. for many applications, including braille dots. It will be understood that such dimensions may be otherwise modified to form desirable design or written characters.

The stencil plate can be any rigid or flexible material which simulates a silk screen in that certain portions prevent passage of the resin mixture whereas other portions permit passage therethrough to an underlying surface. It has been found that certain resin films such as polyester may be employed as a stencil plate as well as metallic plates like brass shim stock. Resin films and softer materials may have cutouts formed in any one of many convenient ways such as with a cutting tool, a heated element, and the like. The more rigid plate such as the brass shim may have cutouts made with sharp cutting tools such as drills, or by acid etching, and the like. It is also intended that certain materials may have cutouts formed through a process of photo-etching in which a resin film or the like with sensitized material is exposed to image formation by the action of light, and in which unexposed portions are removed by appropriate spray wash out. Such unexposed portions will form the openings or the cutouts through which the resin mixture is forced.

The thixotropic paste is spread over the stencil plate by pressure means such as a roller or squeeze blade, and the various openings are filled with the resin mixture. The height of the raised printed character will be substantially as great as the depth of the opening which will be filled with the help of the pressure means.

The following examples are presented to illustrate various ways to practice the invention but it should be understood that such examples are not intended to represent exclusive embodiments of the invention.

In each of the following examples, heat curing was attained by placing the paper with deposited raised printing three to six inches below a heating source in an infrared heating unit manufactured by Comac Engineering Inc., of Byron, Conn. The elements have a power output of 1950 watts. The paper may be placed on an endless belt below the heat source, and such belt may be driven by a motor with a reduced gear train. Rollers at the opposite end of the belt may have cog wheels at their opposite ends to positively drive the belt. The belt may be stopped to hold a sheet under the infrared lamp for a selected time period.

Example 1.—Polyester simulated silk screen

A polyester sheet about 0.008" thick (Dupont, Mylar) was supported on a rigid sheet of hardboard (tempered Masonite). A plurality of holes were placed in the film by using a No. 51 drill (0.067" diameter). The drill was used to make eight groups of holes with each group having an overall rectangular configuration with four rows of four holes per row. The holes were spaced at a distance of 3 mm. gauged center to center in each group. The distance between the groups was about 13 mm. vertically and about 5 mm. horizontally. The film with the holes was mounted in a silk screen frame with adjustable tension means and such simulated silk screen was used as a stencil in some of the subsequent examples.

Example 2

A mixed resin paste was prepared by combining the following ingredients.

Ingredients:	Amounts, grams
Phenolic resin, Resin ST 5085-2A (Schenectady Chemicals Inc.)	2.7
Water	3.0
Vinyl acetate copolymer dispersion, Gelva emulsion TS-100 (Shawinigan Resins Corp.)	1.0

The above ingredients were mixed and the mixture was squeezed with pressure roller means through the openings in the film prepared according to Example 1 onto an underlying sheet of paper. The paper was of newsprint quality, and immediately after the mixture was laid down the paper was removed and placed 6 inches below the Comac infrared drier for about 10 seconds. The distinct, hardened dots which were formed were securely attached to the paper, but were not raised too much. Additions of 2% of a blowing agent (Kemsel, A 9080 paste, Claremont Polychemical Corp.) to the above formulation results in raised dots of good quality when printed through the stencil plate.

Example 3

Ingredients:	Amounts, grams
Epoxy resin, Epon 812 (Shell Chemical Corp.)	6
Curing agent, Gemamid 250 (General Mills)	4

The above type of resin was combined with the curing agent which is believed to be an amine-amide combination. The paste mixture was laid onto newsprint type paper and calender plate type paper by using a squeeze blade to force the mixture through the openings in a polyester film prepared according to Example 1. The papers were cured under infrared heat as in the previous examples, and distinct, hardened dots were formed which were securely attached to the papers. The formed dots were of somewhat reduced height due to a slight spreading on the paper. The mixture was similarly pressed through the polyester film, prepared according to Example 1, with the help of a squeegee blade, and the paper with the deposited resin was cured under the infrared light source for about 10 seconds. The raised, printed dots were of excellent quality; they were hard, tough, and securely adhered to the paper.

Example 4

Ingredients:	Amounts, grams
Epoxy resin, Epon 812 (Shell Chemical corporation)	6
Curing agent, Genamid 250 (General Mills)	4
Huber HT clay	1

The clay was added as a filler or thickener to retard the small amount of spreading which occurred with the formulation of Example 5. The filler tended to make the mixture thixotropic so that it was flowable when being worked, but was not flowable after deposit on the paper. The mixture was similarly pressed through the polyester film, prepared according to Example 1, with the help of a squeegee blade, and the paper with the deposited resin was cured under the infra red light source of about 10 seconds. The raised, printed dots were of excellent quality; they were hard, tough, and securely adhered to the paper.

Example 5

Ingredients:	Amounts, grams
Epoxy resin, Dow DER 667	6
Xylene	15
Curing agent, Genamid 250	4

The solid resin and the xylene were heated and mixed. To the cooled mixture was added the curing agent. The mixture was then pressed through the openings in the simulated polyester film of Example 1 and onto calendar plate paper. The dots were cured under the Comac heater for about 10 seconds whereupon they were distinctly formed, were tough and were securely attached to the paper.

Example 6.—Brass shim plate as simulated silk screen

A brass plate which was 0.012" thick was placed between two like brass plates, and groups of holes were made through the "sandwich" in the manner of Example 1. An excellent grade stencil with clean openings was prepared by this procedure. This plate was used as a stencil for laying down printed dots on underlying sheets of paper with the help of a squeegee blade. Such a plate is adapted to resist deformation from the action of the squeegee blade.

Example 7

Ingredients:	Amounts, grams
Epoxy resin, Dow DER 667	6
Methyl "Carbitol"	10
Curing agent, Genamid 250 (General Mills)	4

The solid resin was dissolved in the solvent with the air of heat. The curing agent was added and the mixture was prepared according to Example 6 with the aid of a squeegee blade. Dots of raised resin were deposited having a height corresponding generally to the thickness of the shim plate. The mixture was applied on newsprint type and calendar plate type papers which were heated for 10 seconds under the Comac infra red drier. Good quality printing was attained on both sheets in that the dots were distinct, tough and securely attached to the paper. The dots in the newsprint type paper tended to be flattened rather than spherical, and were not raised markedly due to the small thickness of the shim plate. Greater penetration into the porous paper may also account for the somewhat flattened dots.

Example 8

Ingredients:	Amounts, grams
Epoxy resin, Dow DER 667	6
Methyl "Carbitol"	10
Curing agent, Genamid 250	4

The above ingredients were processed and mixed as in Example 9, and squeezed through the openings of the brass plate. The deposited resin dots were air dried. The printing was of good quality but showed a slight flattening.

Example 9

Ingredients:	Amounts, grams
Epoxy resin, Adhesive A–31, part A (Armstrong Products Co., Inc.)	15
Curing agent, part B	10

The above resin system is supplied as a thixotropic paste. The mixture of parts A and B were squeezed through the holes in the brass shim plate with the help of a pressure roller. The mixture was laid on newsprint papers. One sheet was heated under the Comac infra red drier and the other sheet was air dried. The mixture was pressed through the brass shim stock onto two additional sheets of calendar plate quality paper, one of said sheets being heated under the Comac infra red drier and the other sheet being air dried. Excellent printing quality occurred on all of the sheets of paper, which quality was graded by distinct, tough dots which were securely attached to their respective papers.

The four sheets having printing on one of their sides were again printed on the reverse sides with the same mixture. One calendar plate and one newsprint type sheets were both cured under the Comac infra red drier and the other pair were air dried. All the sheets had good quality printing on both sides. In each case, the newsprint type paper showed some slight soaking through the paper, but no spreading of the deposited resin.

Example 10

Ingredients:	Amounts
Epoxy resin, Adhesive A–31, part A (Armstrong Products Co., Inc.)	grams 15
Part B	do 10
Isoparaffin, Isopar M (Humble Oil Company)	percent by weight 1

The above mixture Isopar M is an essentially odorless, relatively high-boiling, narrow-cut isoparaffinic. According to the supplier, Humble Oil Refining Company, the solvent has an average molecular weight of 177 and the following volume percent of hydrocarbon types: isoparaffins 80; normal paraffins, less than 0.5; total paraffin, 80. The total naphthenes in volume percent are set at 19.7 and include

16.2 of 1-ring; 3.2 of 2-rings; 0.3 of 3-rings; and none of 4-rings. The monoaromatics are said to be at 0.3 volume percent. Other physical characteristics are set out by the manufacturer in Data Sheet DG–1P was pressed through the brass shim plate with the aid of a squeegee blade. The Isopar M functions as a blowing agent in the mixture. The sheet of paper receiving the mixture was immediately placed in the Comac infra red drier and excellent quality printing resulted. All the dots were distinct, tough and securely attached to the paper. There was no undesirable spreading of the resin mixture. The raised character was higher than the cured characters formed without a blowing agent.

The mixture was again printed on the reverse side of the paper. The sheet was immediately cured in the infra red drier with the same excellent results.

Example 11

Ingredients:	Amount
Epoxy resin, A–31, part A (Armstrong Products Co., Inc.) ____grams__	15
Part B ____do____	10
Blowing agent, Kemsel, A9080 Paste (Claremont Polychemical Corp.) ____percent by weight__	2

The above mixture was forced through openings in the brass shim stock with the help of a squeegee blade and deposited on the one side of a sheet of calender plate quality paper. The paper was dried under the Comac infrared drier and the printing was of excellent quality with no spreading. All the dots were distinct, tough and securely attached to the paper, and at a raised height greater than the thickness of the brass shim stock. The primary component of the Kemsel blowing agent is azodicarbonamide as identified by the manufacturer, Claremont Polychemical Corporation of Roslyn Heights, N.Y.

The dots printed in Example 9 without the blowing agent, averaged a height of about 11 mils when dried under the infrared drier. The average height reached of the printed dots when air dried was about 10 mils. The heights of the printed dots were substantially the same whether newsprint or calender plate type paper was used, except there was a slight tendency of the printed dots to be higher on the calender plate type paper. When 1% Isopar M was added, as in Example 10, to the formulation, the height of the printed dots on the calender plate type paper averaged about 18 mils. When the concentration of Isopar M was raised to 2% in the A–31 formulation, the height of the dots averaged about 15 mils, or substantially very little change. No substantial change in the height of the dots was observed even after the resin concentrations of Isopar M were increased to 5%.

The formulation which contained 2% of the Kemsel blowing agent (Example 11) resulted in formed dots having a height which averaged about 23 mils on calender plate type paper.

Example 12

Ingredients:	Amount
Epoxy resin, A–31 formulation, part A (Armstrong Products Co., Inc.) ____grams__	15
Part B ____do____	10
Blowing agent, Kemsel K–9080 paste percent by weight__	2
Dutch Boy Dyphos (National Lead Company) percent by weight__	2

The Dutch Boy Dyphos is a lead compound which lowers the decomposition temperature of the blowing agent so it may be activated by a lower temperature. The above mixture was forced through the holes in the brass shim stock with the help of a squeegee blade, and the resin dots were printed on the side of a calender plate type sheet of paper. The paper was then placed under the Comac infrared drier for 10 seconds, whereupon excellent quality printed dots were formed averaging about 23 mils in height. All of the dots were spherical, tough, and securely attached to the paper.

Example 13

Ingredients:	Amounts, grams
Urethane resin, Uralane 1723–6–A (Furane Plastics Corp.)	59.3
Urethane curing agent, Uralane 1723–6–B (Furant Plastics Corp.)	53.4

The above ingredients were mixed and the mixture was pressed through the holes in the 12 mil brass shim stock, prepared according to Example 7, with the help of a squeegee. The dots on the paper were allowed to air dry, and after aging 24 hours were substantially free of tack. Each dot was raised and tests showed that the height of the dots averaged about 11 mils.

Example 14.—Photographically etched resin film

A resin sheet supplied under the name of Dycril by the Du Pont Company of Delaware is a photopolymer sensitized sheet on which various patterns are formed as a stencil after conventional light sensitization and development. The 12 mil thick film was processed so that a plurality of unexposed randomly distributed small areas were washed away to form a plurality of openings. One edge of this film was attached to the edge of a glass plate, and a sheet of paper was inserted under this stencil film.

The following two formulations were prepared and separately forced through the various openings onto the underlying sheets.

FORMULATION NO. 1

Ingredients:	Amounts, grams
Epoxy resin, A–31, part A (Armstrong Products Co., Inc.)	7½
Part B	5
Blowing agent, Kemsel, K–9082 paste (Claremont Polychemical Corp.)	0.2

The sheets with the deposited dots were cured in the Comac infrared heater for short periods of time, whereupon small raised dots were formed which were hard, tough and securely attached to the sheets of paper.

FORMULATION NO. 2

To Formulation No. 1 the following ingredient was added.

Ingredient:	Amount, grams
Carbon powder, Statex (Columbia Carbon Company)	0.2

This mixture was forced through the photo film stencil in the same way as with Formulation No. 1. Hard, distinct, black raised dots were printed on the paper.

Example 15

Ingredients:	Amounts, grams
Polyester resin, Koplac resin D3000–1500 (Koppers Company)	20
Benzoel peroxide	0.2
2-ethyl hexyl acrylate	15
Carbon powder, Statex (Columbia Carbon Company)	5
t-Butyl-peroxy pivalate, Lupersol 11 (75% in mineral spirits)	0.5

The acrylate is a monomer more reactive than the polyester. The acrylate was mixed with the peroxide which is a low temperature catalyst and with the pivalate which is a high temperature catalyst. This combination extends the pot life of the resin mixture. The polyester resin was then added, and the carbon powder was stirred in last. The mixture was forced through the openings in the 12 mil thick brass stencil prepared according to Example 7, and the sheets were cured in the Comac infrared drier (1,950 watts) for 15 seconds. The dots were black, hard and raised, but were characterized by slight spreading.

Example 16

Ingredients:	Amounts, grams
Polyester resin, Koplac resin 1580–5	20
Cumene hydroperoxide	0.8
Blowing agent D–800 (Lucidol Division of Wallace-Tiernan)	0.4
Silica, Cab-O-Sil (Godfrey L. Cabot Co.)	0.15
Carbon powder, Statex (Columbia Carbon Company)	0.2

The polyester was mixed with the peroxide which is a high temperature catalyst, with the blowing agent and with the Cab-O-Sil filler which is a high surface area silica. The blowing agent B–800 is identified as diisopropyl azodiformate by the manufacturer. The carbon powder was added last. The mixture was forced through the openings in a 12 mil thick brass plate prepared according to Example 7. The paper was cured at 3 inches from the Comac infrared heater for only three seconds so that no scorching would occur. Light grey dots were formed which were securely attached to the paper.

Example 17

Ingredients:	Amounts
Phenolic resin, Plenco No. 677 resin (Plastics Engineering Co.)	grams 9
Curing agent, Hexamethylenetetramine (Du Pont)	gram 1
Blowing agent, Kemcel A–9080 paste (Claremont Polychemical Corp.)	percent by weight 1

The above type of resin was combined with the curing agent and laid onto newsprint type paper and calender plate type paper by using a squeegee blade to force the mixture through the openings in a polyester film prepared according to Example 1. The papers are cured under the Comac infrared heater, and distinct, raised, hardened dots are formed which are securely attached to the papers.

Example 18.—Brass shim plate as simulated silk screen

A twelve mil thick brass plate is processed with stamping tools by which various block and script letter cutouts are formed in the plate. The dimension of the lines in each letter are about 1½ mm. The height of the letters vary from 3 mm. to about 5 mm. The resin mixture of Example 12 is prepared and forced through the letter cutouts with a squeegee blade. The brass plate is removed and the paper is cured under the Comac infrared drier. The raised letter printing is distinct, tough, hard and securely adhered to the paper.

Addition of 0.2 gm. of carbon powder to the formulation of Example 12 forcing such mixture through the brass plate with the letter cutouts results in black raised printing after curing the deposited resin characters.

The various embodiments of the foregoing examples disclose improved quality raised thermosetting resin printing. The raised nature of the printing is the desired quality together with the other properties of paper adhesion and toughness. The actual height of the resin characters can of course be widely varied to meet and satisfy particular demands. The raised printing is effectively accomplished by using the epoxy resins and other thermosetting resins with blowing agents. The height of the raised character is at least partly controlled by the depth of the cutout in the stencil plate. A raised character formed from an epoxy without a blowing agent will have a height corresponding substantially to this depth, although in some instances it may be slightly less due to the occasional possibility of some resin spreading. In such an event, presence of the blowing agent will raise the printed character to the depth of the cutout, or even higher. The important feature is that the height can be controlled by incorporating into the resin—optionally with epoxies and conventionally with other thermosetting resins—a small amount of a blowing agent. The term "blowing agent" is intended to cover those known and available materials which lead to intumescence or puffing of a material to which it is added. This is customarily accomplished by release of nitrogen or carbon dioxide. Such agents are known and can be incorporated into various thermosetting resins in the manner taught in preceding portions of this disclosure.

The feature of intumescence has been found to be important for thermosetting resins generally and, optionally, for the epoxy resins. A good quality raised printed character is necessary for the successful practice of the invention, and an important step of the process requires that a stencil plate be used to effect such a raised, printed character. The stencil plate is, of course, placed in abutting relationship or contact with the paper so that the thixotropic paste in the cutouts is cleanly in contact with the paper within the confines of the cutout configuration. The term "cutouts" through this disclosure is intended to cover any type of opening in the plate irrespective of the manner in which such opening was formed. The term "plate" is intended to cover operable simulated silk screen materials, whether flexible, rigid, metallic, resinous or other. Several embodiments of a stencil plate have been disclosed, and it will be apparent that many additional embodiments could be devised within the silk screen principle. The illustrated embodiments have described a batch type process for depositing raised, printed thermosetting characters on a sheet of paper, but it will be appreciated that a continuous process could be devised in obvious ways by those skilled in the art to practice this invention. This could involve curved stencil plates to reciprocally engage a sheet of paper either on a supporting surface to print one side at a time, or between a pair of curved stencil plates to simultaneously engage the reverse sides of a sheet of paper. Appropriate mechanized or automated means may be provided to feed sheets of paper into contact with the stencil plate or plates, to activate the stencil plates, to transfer the resin mixture onto the plate, to force the resin mixture through the cutouts or openings and to cure the deposited, raised resin characters on the paper.

The amount of resin placed on the plate need not be metered in any strict sense because it is merely necessary to have enough to conventionally fill the cutouts in the plate. Practitioners will know that the actual amount placed on the plate will be a workable amount—enough to fill the cutout and not unduly superfluous so the operation becomes messy.

Reference has been made to "printed character impressions" or "printed" in various places of this disclosure. These terms are intended to have a broad meaning in so far as they pertain to the present process. In such a context "printed character impressions" shall refer to the raised, resin impressions which are applied to the surface of paper by forcing a thixotropic paste mixture through the cutouts or openings in the stencil plate.

Various types of paper may be used to receive the raised, thermosetting printing and reference to "paper sheet" is intended to include different thicknesses of paper with different qualities of coatings or finishes. This term will also include cards, cardboard, tissues, onion skin, newsprint, calender plate and other cellulose fiber base materials commonly included within the generic meaning of "paper." With absorbent papers such as newsprint there may be some tendency towards spreading of the deposited resin characters, but this can at least be partly counteracted by incorporating the blowing agent and fillers. With higher quality papers which are coated and calendered, the likelihood of spreading is not present to the same extent.

The cheaper newsprint type paper can be used to advantage to quickly print braille character impressions, and this can be done on both sides of such paper. Better quality paper can be used for this purpose in order to

provide a permanent record available for repeated readings. Better quality papers will be used for business cards and letterheads, and heavier grade papers can be used for greeting and holiday cards. In addition to the intelligible characters, such as letters, which can be deposited, esthetic patterns can also be applied. Reference to "character impressions" is intended to cover both these concepts.

The foregoing invention can now be practiced, and such practitioners will know that the invention is not necessarily restricted to the particular embodiments presented herein. The scope of the invention is to be defined by the terms of the following claims as given meaning by the preceding description.

I claim:

1. A paper article with raised intelligible printing which includes,

a sheet of paper,

intelligible characters of a hard, non-resilient, and cured thermoset resin securely bonded to the surface of said paper,

said hard cured thermoset resin characters having a substantially uniform mixture which consists essentially of a thermosetting resin, a curing agent for said resin, a thixotropic filler, and a decomposed residue of an added blowing agent,

said blowing agent having been added to said resin in its original condition in an amount sufficient to substantially raise the resin character, above its height as originally deposited on the surface of the paper, and

said resin characters being distinctively contrasted with such sheet of paper so as to be readily perceptible.

2. A paper article as in claim **1** where said intelligible characters are letters, and wherein the thermosetting resin is an epoxy resin.

3. A paper article as in claim **1** wherein the intelligible characters are in the form of selected block or script letters.

4. A method for printing hard, non-resilient raised intelligible and cured thermoset characters onto the surface of paper which includes,

preparing a resin mixture which will be distinctively contrasted on said paper, said resin preparation consisting essentially of a substantially uniform mixture of a thermosetting resin, a curing agent for said resin, a thixotropic filler, and an added blowing agent in an amount which will raise the printed character on the surface of the paper,

placing a stencil in contact with a surface of a sheet of paper,

forcing the resin mixture through cutouts in the stencil placed on the surface of said paper, said cutouts conforming to the desired configuration which the raised and intelligible characters will assume on the surface of the paper, the height of the raised impression which will be placed upon the paper being at least as high as the thickness of the stencil,

removing the stencil, and

curing the resin on the surface of said paper under conditions to activate said blowing agent to form hard, raised thermoset characters which are securely bonded to the paper.

5. A method as in claim **4** wherein the thermosetting resin in the resin mixture is an epoxy resin, and said resin mixture is forced through cutouts having the configurations of letters.

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