

1

3,440,076

RAISED PRINTING PROCESS

Frans V. E. Vaurio, Appleton, Wis., assignor to Fox River Paper Corporation, Appleton, Wis., a corporation of Wisconsin

No Drawing. Filed Nov. 12, 1965, Ser. No. 507,520

Int. Cl. B44d 1/14; B41m 5/26

U.S. Cl. 117—13

6 Claims

ABSTRACT OF THE DISCLOSURE

The method of forming raised hard printed characters on a sheet of paper. An ink composition is printed on the paper and then contacted with a dry material. One of the ink composition and dry material contains a thermosetting resin and the other contains a blowing agent and a curing agent. The dry material not adhering to the ink is removed and the resin associated with the printed character is then cured.

This invention relates to a method of providing improved raised hard printing; it further relates to a paper product having such printing.

The printing art has long practiced raised printing on paper by a method other than engraving. A principal method is known as thermography and a well known commercial practice is the Virkotype process. This process is more economical and less complicated than engraving printing. Such printing has been performed on business forms, letter heads, business announcements, wedding invitations, greeting cards, and the like.

In thermography, printed characters are applied on a sheet of paper in the usual letter press or offset process. While the ink remains moist, a powdered mixture is sprinkled or dusted over the printed ink. The powder not present on the printed ink characters is removed, and the powdered mixture adhering to the still moistened ink is then fused by exposing the printed characters to a heat source at temperatures sufficient to fuse the powdered mixture but not to burn the paper. This fusion is characterized by a slight raising action which results in the characteristic raised printing of the Virkotype process, for example. The powdered mixture is believed to be essentially a rosin material, that is, an abietic acid containing material.

It is desirable to improve the process with respect to the degree of adhesion of the raised printed character to the sheet of paper, and to extend the applicability of the process so that the reverse sides of a single sheet of paper can be printed with such raised characters. The powdered mixture used in the conventional thermographic process is not heat stable and, therefore, a sheet of paper having raised characters on one side cannot be exposed to the fusion temperatures lest the already fused character deteriorates under the application of heat.

It is also desirable to selectively attain various heights of the raised characters to meet different requirements which may arise in the art. In the thermographic process the "raise" of the printed characters is unduly limited in that only the inherent nature of the rosin controls the degree of the attained height.

In view of the foregoing discussion it will be appreciated that a desirable object would be an improved raised printing wherein the printed characters are securely bonded to the paper, are heat stable, and have their height more or less selectively regulated. Such is a principal object of this invention.

Another object is a method where printed characters of various types can be provided with all the advantages of the thermographic process, plus additional advantages

2

without substantial increase in cost or increase in the number and complexity of the manipulative steps.

Another object is an improved method for raised printing in which heat stable printed characters are formed on a sheet of paper.

Another object is a method whereby raised printed characters are formed on a sheet of paper with improved attributes of the raised characters.

Another object is a raised printed character wherein an improved level of raising is attained with modest amounts of a powdered mixture, yet attaining a printed character which is securely bonded to the paper and is heat stable.

Another object is a sheet with printed characters in which the printed characters are heat stable and are present on opposite sides of the same sheet of paper.

Another object is a printed sheet wherein the printed characters are formed in a desirably raised manner by a powdered mixture which has been rendered heat stable under fusion temperatures.

All the objects which have been recited are attained together with other objects not mentioned, but which will become apparent from considering the invention in the following disclosure.

The conventional thermographic process has now been markedly improved by applying a powdered mixture to the moist printed ink which may contain a curing agent. The mixture consists essentially of a thermosetting powder, or consists essentially of a thermosetting powder having mixed therein a small amount of a blowing agent, or consists essentially of a blowing agent. A thermosetting powder sprinkled on the moistened printed character will rise to some extent when subjected to heat fusion. This rise will understandably be limited by the properties of the thermosetting resin, but, nonetheless, will occur. Such a raised printed character has desirable features and, following fusion, the hard printed character is securely bonded to the paper in an improved manner and is heat stable in an improved manner. The heat stability is far above the desired level in that like raised printing can be formed on the same sheet of paper under subsequent exposure to fusion temperatures without deteriorating the previously fused printed characters on the same sheet.

It has been found, however, to be a preferred practice to include into the resin powder a small amount of dry blowing agent such as a nitrogen evolving compound. This small amount of blowing agent may be present practically from about 1 percent to about 5 percent by weight of the thermosetting powder or powdered mixture. This is an operable range which is preferred since a blowing agent in an amount substantially less than 1% will have very little desirable raising effect. Blowing agent in amounts substantially greater than 5% will tend to result in a printed character containing an undesirable number and size of voids, therefore presenting the hazard of friability. Various blowing agents known to the art may be incorporated in such a preferred range, and they include the azo-bis nitriles and the carbon dioxide evolving solid blowing agents. Other agents known to the art will be operable.

The thermosetting resin materials are those which can be fused under heat levels which are not damaging to the paper. The thermosetting resin is preferably fused or cured by the action of a curing agent in the ink. It will be appreciated that different levels of heat can be used with different paper depending on the thickness and strength of the paper, and the like. Heavier papers which are used for business announcements, for example, can be exposed to greater heat fusion levels than thin stationery bond. The thermosetting resins have been found to make

excellent hard raised printed characters and to retain the property of hardness and heat stability. Representative resins are the polyesters, the phenolics, the various formaldehydes including phenol, urea, melamine and aniline; and the epoxies. The printing ink will preferably contain the appropriate curing agent or agents for the respective thermosetting resins. Such are well known in the art.

All these resins can be springled or dusted onto a sheet freshly printed with printing inks which are substantially nondrying. Such inks may be oil base inks or other, and include conventional printing inks used in offset or letter press printing. Such inks have a resin, oils, drier, solvent and pigment. They are compounded according to well known procedures which are described, among other places, in *Manufacture of Printing and Lithographic Inks* by Herbert J. Wolfe. High-gloss letter press inks have been used in thermography. Such an ink has been described in the *Chemical Formulary*, vol. x, 1957 by H. Bennett.

It has been found that alternative ways to practice the invention are possible with inks containing aromatic organic solvents. The thermosetting powder may be incorporated into the ink composition by being dissolved in the solvent and, possibly, the oils. When such a prepared ink is laid down, the dry curing agent, with or without blowing agent, may be sprinkled over the printed characters. The heating temperature will then more expeditiously fuse and cure the resin because of the curing agent. Likewise, the curing agent may be dissolved in the ink and the thermosetting resin, containing a blowing agent, sprinkled thereon. Other combinations may be included with the ink, such as blowing agent and resin, whereupon curing agent alone is springled thereon; and curing agent and blowing agent, whereupon thermosetting resin alone is sprinkled thereon. The curing step has been said to be performed under a fusion temperature with a curing agent generally; however, in some applications the practitioner may consider a raised printing formed without a curing agent to be satisfactory for his purposes. It is possible for other curing steps to be practiced such as providing an atmosphere to induce cross linking, for example, boron trifluoride; impinging high frequency waves in the resin; and irradiating the resin. Practitioners know that the foregoing procedures can be successfully practiced under certain conditions and with certain provisions.

The substantially nondrying inks containing the curing agent can be applied with the conventional offset or letter press printing. For more porous papers it may be desirable to increase the amount of ink so that moistened ink character remains on the paper to receive the powdered thermosetting mixture.

Various heat sources may be used to provide a fusion temperature such as electric or gas heaters. It has been found that a highly successful heat source is an infrared heating unit manufactured by Comac Engineering Co., of Byron, Conn. The elements of such a heater have a power output of 1,950 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 to positively drive the belt. The belt may be stopped to hold the sheet under the infrared lamp for a selected time period to fuse the thermosetting powdered mixture.

The following examples are presented to illustrate various embodiments of the invention, but it should be understood that such examples are presented to teach the invention rather than to represent exclusive embodiments.

EXAMPLE I

A sheet of paper is printed in a hand letter press type with conventional thermograph ink containing an epoxy curing agent on stationery bond paper. Immediately after printing, epoxy resin powder is dusted and sprinkled over

the entire sheet of the paper to assure contact between the printed characters and the thermosetting powdered mixture. The paper is then agitated gently by finger tapping to remove the excess thermosetting powder mixture not adhered to the raised printed character. The sheet is then placed on the belt of the Comac infrared heater about 6 to 12 inches below the heating element and exposed thereto for about 10 to 15 seconds. The raised printed characters are fused into a hard raised character securely adhered to the paper.

EXAMPLE II

A paper is printed as in Example I, except that the ink contains an effective amount of hexamethylene-tetramine and the thermosetting resin mixture consists essentially of phenolic resin sold under the trademark Resin SP5085A by Schenectady Chemical Inc. The excess resin is removed as in the previous example, and fused under the infrared element.

EXAMPLE III

Dow DER 667 thermosetting powder is combined with 2% of a nitrogen evolving blowing agent, Kemsel, 9080 (Claremont Polychemical Corp.), and the combined mixture is sprinkled on a printed sheet of paper prepared according to Example I, except that the curing agent in the ink is Genamid 250 (General Mills). Dow DER 667 is the trademark for the epoxy resin sold by the Dow Chemical Company and which is the soluble resinous reaction product between Bisphenol A (4,4'-isopropylidene diphenol) and epichlorohydrin, having an average molecular weight in the range of 3,200-4,000, and disclosed in U.S. Patent 3,140,959. Kemsel 9080 is the trademark for the dispersion of 60% azodicarbonamide and 40% vinyl plasticizer sold by Claremont Polychemical Corp. Genamid 250 is the trademark for fatty amino acid sold by General Mills. The excess resin is removed and the thermosetting powdered mixture adhered to the printed character is fused under the infrared heat element. Hard printed characters securely adhered to the paper are raised substantially higher than the raise in previous Example I.

EXAMPLE IV

The paper with the raised printed characters on one side, prepared as in previous Example III, is again printed on the reversed side with the same ink. The same resin mixture as in previous Example III is then applied. The excess is removed and the paper is again submitted to an infrared heat source until fusion of the newly applied thermosetting resin mixture is effected. The hard raised characters previously formed on the obverse side are not altered or deteriorated in any way by the second heat treatment.

EXAMPLE V

To the paper printed according to Example I, where the ink contains hexamethylene-tetramine, a thermosetting resin mixture is applied which consists essentially of phenolic resin sold under the trademark Plenco 677 by the Resin Plastic Engineering Company, and 1% of a blowing agent, Kemsel A9080. The paper is treated as in the previous examples to obtain hard raised characters securely attached to the paper.

EXAMPLE VI

A thermographic printing ink is compounded from the following ingredients:

Ingredients:	Parts by weight
Modified phenolic resin	24.69
Raw linseed oil	26.03
Regular No. 1 linseed oil	26.03
High boiling petroleum solvent	16.38
Chlorowax 70	6.12
Cobalt napthenate (6%)	0.75

The Chlorowax 70 is the trademark for a liquid resinous chlorinated paraffin sold by the Diamond Alkali Company and having the following properties: Sp. gr. 1.6-1.7; M.P. 90-100° C. The cobalt naphthenate operates as a drier. Into the foregoing compounded ink composition is added about 2% of nitrogen evolving blowing agent, Kemcel A9080, and about 5% of diethylene triamine curing agent. The ink composition is mixed until the additives are thoroughly incorporated. This ink composition is printed on paper as in Example I, and then epoxy powder is dusted on the paper. The paper is processed and heat cured as previously described.

EXAMPLE VII

To the ink composition of Example VI is added epoxy resin in small amounts with vigorous mixing. The excess resin not dissolved is separated and the ink composition is printed on paper as in Example I. Onto the moistened printed characters is applied a mixture of 10% sodium bicarbonate and the balance, dimethyl amino methyl phenol.

EXAMPLE VIII

To the ink composition of Example VI is added about 10% of the dihydric alcohol, glycol. The composition is printed on paper as in Example I, and a mixture is applied to the printed characters. Such mixture is about 10% of blowing agent (Kemcel A9080) and the balance terephthalic acid. After the excess mixture is removed, the paper is subjected to heat below the char level of the paper to obtain the cured polyester.

Reference has been made to an essentially batch process for preparing the improved raised printing but such method is clearly adaptable to semi-continuous or continuous operations. Equipment is provided for reclaiming excess powder by vacuum treatment, such machines are further equipped with dome gas heaters to provide the fusion temperatures for the deposited thermosetting resin. Such machines are generally known as embossographers and are supplied by the Embossograph Process Company, Inc., of Brooklyn, N.Y.

Reference has been made to the conventional inks which are, of course, rendered black by inclusion of carbon powder. Other color inks may be obtained, or even clear inks were desired. Metallic powders may be added to ink to provide a lustrous metallic effect such as with gold, silver or copper. Opaque colors may be added such as pink, red, yellow, green or even opaque white. Likewise, fluorescents, powders, sparkle powders and glitter powders may be compounded according to skills recognized in the art.

By the present improved process, the hard raised images or characters are obtained by combining a properly controlled ink application step with a sprinkling powder deposition or dusting step. In this last step, a thermosetting resin can be applied alone, a blowing agent can be applied alone, a curing agent can be combined alone or various mixtures thereof. It is required that in the dusting step the mixture be not tacky or liquid so the excess may be removed from the paper without defacing the paper. The thermosetting resin powder can be added during the sprinkling step alone and then fused by the curing step which may be heat, irradiation, high frequency or the line. It is a preferred practice to apply fusion temperatures below the char level of the paper.

The present invention permits various ways to practice the steps which increases versatility and leads to advantages of different ways of handling. Any one or more blowing agent, thermosetting resin, and curing agent may be incorporated in the ink composition and then subjected to curing. It is preferred to use one of the curing agent or thermosetting resin in either the ink application step or the dusting step and the other of said two materials in the other step. Mixing a curing agent and thermosetting

resin undesirably shortens pot life, but even this method may be practiced by taking recognized precautionary steps to prolong the pot life or to, alternatively, quickly practice the step of printing the ink composition on the paper. When applying the epoxies, the common primary, secondary and tertiary amines may be employed as curing agents. Curing agents which are powders at or near room temperatures are of course preferred. A liquid curing agent may, however, be used and incorporated in the ink composition while the dry epoxy is added during the dusting step.

The amounts of thermosetting resin added to the ink composition is preferably an excess so that as much is dissolved or suspended as possible. Any excess can be easily separated by a decanting, precipitation or the like. An amount of curing agent and blowing agent to be added in either the dusting or ink application step can be readily determined by those skilled in the art to obtain raised characters of certain hardness or certain height. In general, crosslinking curing agents can be easily determined by calculating roughly equivalent stoichiometric amounts, whereas catalytic curing agents are empirically determined by conventional steps which lead to a convenient rate of reaction. Once this convenient rate of reaction is established (not violent or sluggish) the amount of catalytic agent can be varied up to about 50%. Irrespective of whether curing agent is used or not, it is preferred to expose the paper following dusting to a curing step which is preferably a fusion temperature below the char level of the paper. Such fusion temperatures induce better crosslinking of the resin on the raised image or character.

In the sprinkling or dusting step a substantially dry material is deposited on the printed characters or images, and the dry material not adhered to said images is removed in one or more various ways such as agitating the paper by tapping or the like, vacuum removal or blowing.

The finished paper product will have the hard raised images or characters securely bonded to the paper. The hard cured images may include the printing ink and the thermosetting resin alone or printing ink, thermosetting resin and blowing agent; or printing ink, thermosetting resin, blowing agent and curing agent. The blowing agent will of course be in the decomposed state resulting from release of the gas which will generally either be nitrogen or carbon dioxide.

I claim:

1. A method for converting printed characters into hard raised forms which includes the steps of:

printing a character on a sheet of paper with an ink composition,

contacting the sheet of paper having the printed characters with a substantially dry material, one of said ink composition and dry material having at least a thermosetting resin,

removing the dry material not adhered to the printed characters, and the other of said ink composition and substantially dry material having at least a blowing agent to raise the resin while curing and a curing agent, and

curing the thermosetting resin associated with the printed character.

2. A method as in claim 1 further characterized in that the curing of thermosetting resin is facilitated by a fusion temperature below the char level of the paper.

3. A method as in claim 1 further characterized in that the ink contains the curing agent for the thermosetting resin.

4. A method as in claim 1 further characterized by and including a blowing agent in the dry material present in an amount of about 1% to about 5% by weight of said dry material.

5. A method as in claim 4 further characterized in that the blowing agent is a nitrogen evolving compound.

6. A method for converting printed characters into hard raised forms which includes the steps of:

printing a character on a sheet of paper with an ink composition;

contacting the sheet of paper having the printed characters with a substantially dry material, the dry material containing a thermosetting resin and an amount of blowing agent effective to raise the printed character, the ink containing a curing agent for said thermosetting resin, said dry material contacting the paper by freely falling over the printed characters in a dusting step,

removing the dry material not adhered to the printed characters, and

curing the thermosetting resin associated with the printed character, said curing being facilitated by the step of exposure to raised temperatures which are below the char level of the paper.

References Cited

UNITED STATES PATENTS

3,285,802	11/1966	Smith et al.	117—38
3,083,116	3/1963	Berndt	117—13

OTHER REFERENCES

I. Skeist, "Epoxy Resins," Reinhold Plastics Series, 1958, pp. 25-26, 249-251.

C. Ellis, "Printing Inks," Reinhold Publishing, 1940, pp. 234, 397-398.

ALFRED L. LEAVITT, *Primary Examiner.*

ALAN GRIMALDI, *Assistant Examiner.*

U.S. Cl. X.R.

117—25, 38; 106—30