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3,063,864

MATERIAL FOR RECEIVING INSCRIPTIONS AND METHOD OF MAKING

Filed Sept. 28, 1959

2 Sheets-Sheet 1

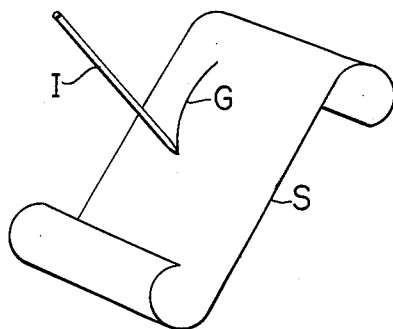
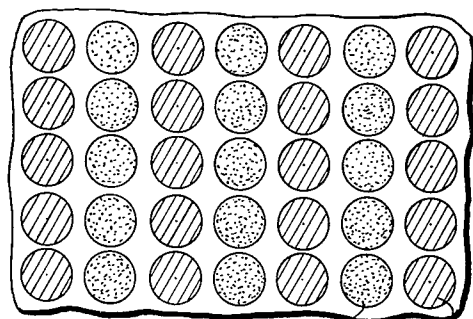
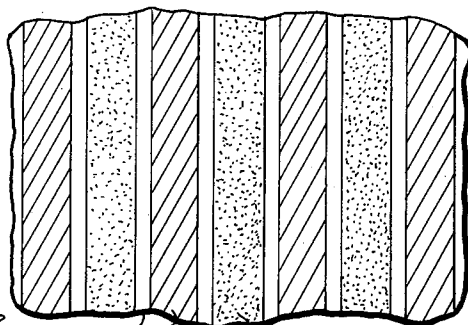


FIG. 1



NO SCALE

FIG. 4



NO SCALE

FIG. 5

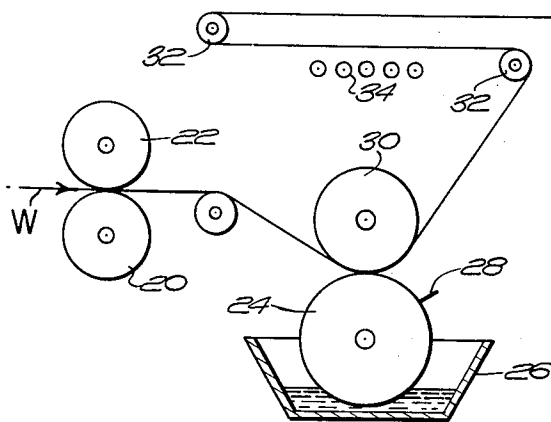


FIG. 6

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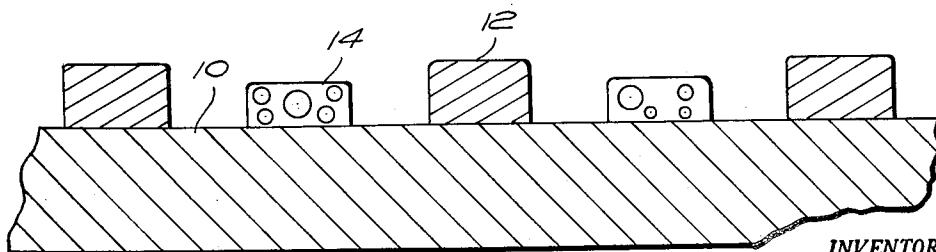
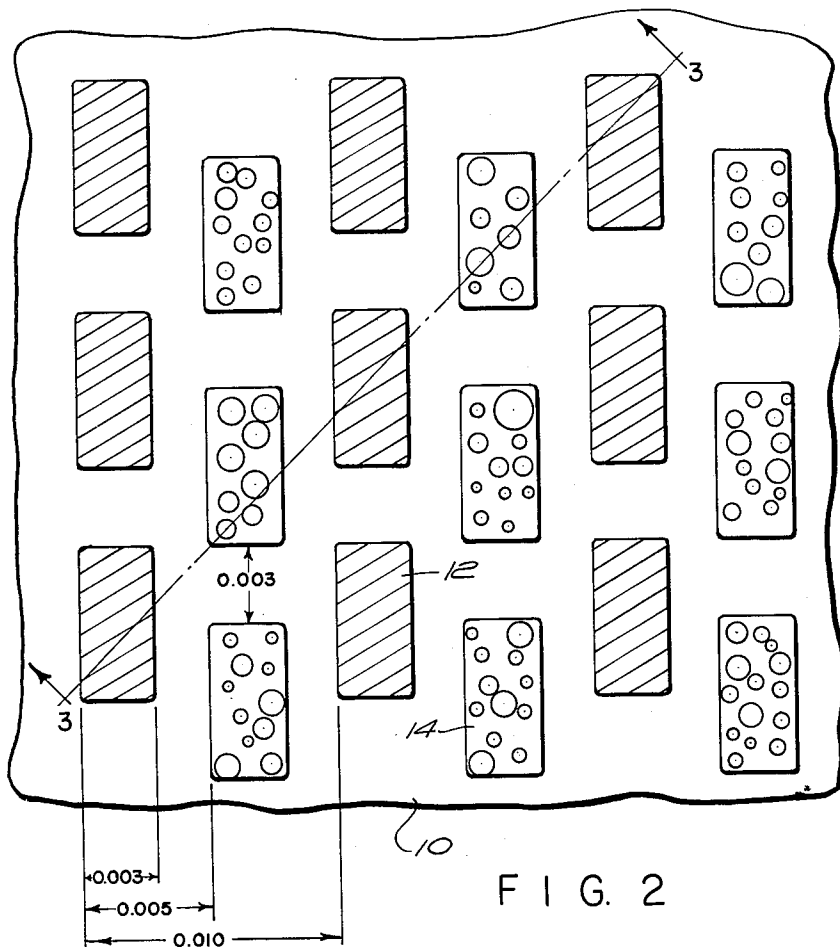
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2 Sheets-Sheet 2



NO SCALE

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3,063,864 MATERIAL FOR RECEIVING INSCRIPTIONS AND METHOD OF MAKING

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10 Claims. (Cl. 117—36.8)

This invention relates to a medium in the nature of a sheet of paper for receiving inscriptions of significant symbols or representations, for instance in the form of lines, and to a method of producing the same. The nature of the product is such that it probably will be most helpful to introduce the description and later explain the details more or less metaphorically and with liberal use of analogies to well known things which are in fact substantially different. It may be said however that the product is a sheet of generally uniform appearance and tone of color, like "a blank sheet of paper" on which is produced an inscription, generally in a contrasting color, by the action of an inscribing instrumentality which may be similar to and operated generally as a pen, pencil or raised piece of type is used on paper, without however the transfer of any ink, pigment or the like to produce the inscription. The inscription may arise from pressure of the instrumentality, from heat transmitted therefrom (or heat and pressure combined) or from the traction of the instrumentality traversing the surface.

The product of the invention may be usefully employed for many purposes. When used under some ordinary sheet of paper or the like it will yield duplicate copies similar to so-called carbon copies, although no carbons are used, provided the original inscription is done by an instrumentality which would produce a carbon copy. Thus the type of a typewriter or the pressure of a lead pencil or of a ballpoint pen or a so-called stylographic pen would make an original on an ordinary sheet of paper, and identical copies on underlying sheets of "paper" embodying the invention. Stamping, as with a metal die of a time stamp or an inked rubber stamp on the original would also be reproduced. Moreover, both an original and copies as above described could be produced by operating the typewriter without any ribbon or writing with a dry stylus for instance, or a ballpoint pen which no longer has any ink in it. Since the writing would immediately appear the act of manual inscription would be as easy and natural as doing it with a pen or pencil. What has been said applies to all types of multicopy business forms such as sales slips, autographic register supplies and so on, wherein interleaved sheets of carbon paper are customarily used.

The paper will not only record the successive typing of letters in a typewriter, but will be affected by the pressure of raised type of a printing plate or form of movable type without any ink being applied to the type. For the production of small runs of work and for the production of books and magazines of ephemeral interest, the use of the material as stock might be advantageous where such printing mechanism is available, since such use would avoid filling and caring for inking mechanisms and the cleaning up job afterwards. In many instances a number of copies of satisfactory quality might be prepared from a single impression of the type form or plate, just as a number of copies could be simultaneously prepared in a typewriter by a single writing, and provide an increased output as compared with the normal operations of simpler types of printing presses, in particular those of the bed and platen type.

The product provides a useful "chart," of circular or strip form for use with all types of measuring instruments wherein the measurement is translated into or indi-

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cated by a movement of some part so that the amount of movement indicates in some manner the value of the variable being measured. It is adaptable both to a linear inscription or one formed by dots.

Since the product operates because of a relationship of its component elements which exists on a very small scale relative to the dimension of the inscribing instrumentality and which may approach the microscopic, or be, in fact, microscopic, it is necessary to illustrate the following description by diagrammatic drawings on an enormously exaggerated scale and to express their relationship by words naturally used and understood with respect to coarser and macroscopical relationships more familiar to ordinary experience, but which it is believed will be suggestive and promote a ready understanding, although they may not carry all the connotations of their commoner usage.

The following specification is illustrated by drawings wherein:

FIG. 1 is a mere graphical memorandum illustrating the production of an inscription on a base sheet by a stylus-like instrument;

FIG. 2 is a diagrammatic plan view of an exemplary form of the invention on an enormously exaggerated scale, as indicated by certain dimensions indicated thereon;

FIG. 3 is a diagrammatic section on line 3—3 of FIG. 2;

FIGS. 4 and 5 are diagrams similar to FIG. 2 showing modifications; and

FIG. 6 is a diagrammatic illustration of a rotary intaglio (gravure) printing press such as may be used in manufacturing the product.

In FIG. 1 I illustrate a partially unrolled scroll S on which we see inscribed a line G which has been formed by the action on the surface of an inscribing instrumentality I in the nature of a "stylus" which has moved from above along the line G to the position shown. In the usual case of manual inscriptions on ordinary paper such a stylus would be a pen with ink or a lead pencil, in each case transferring marking material to the surface of the inscription receiving medium. Similar inscriptions are made in various types of recording mechanisms, such for example as a recording thermometer or thermograph, by pens or by styli which scrape away the surface of the "chart," or which by means of heat or pressure, or both, locally displace or melt a coating on the chart to reveal the contrasting color of its backing. The material contemplated by the invention might serve as such a scroll or chart and be inscribed by a "stylus" although having a more extensive application as will hereinafter be noted. I believe however that it will facilitate understanding if I describe it first in connection with such a stylus inscription, as I shall now do without limiting intention. It should be understood that no ink is used, nor is any functionally equivalent material transferred by the stylus to the record surface.

In accordance with the embodiment of the invention referred to I would usually utilize a base of paper or similar thin sheet material such as metal foil or a film of polyethylene terephthalate (known by the trade designation "Mylar") although the use of rigid bases is not excluded. This base serves as a carrier for the medium by means of which the inscription is formed and recorded thereon, but is inert to the stylus-induced changes in that medium by which the inscription is brought into existence. The desirable qualities to be considered in choosing the base will be obvious to those skilled in the graphic arts. On this base is a coating which to the naked eye is of a uniform character and of apparently uniform color or tone. When a "positive" inscription is desired the base will be of a relatively light tone to contrast with an inscription of darker color. Microscopically however this coating is not continuous. This does not mean merely

that a microscope can identify individual particles existing in an apparently continuous film. The coating consists of minute areas, tiny dots (FIG. 4) or streaks like the filament of a spider's web (FIG. 5) which are very close one to another but yet are separate as isolated individual entities in a geometrical pattern over the area of the backing. I believe that to say that adjacent ones have an air-gap between them will be a concept helpful to understanding. These isolated areas of course have dimensions and a volume, but so small that many common words defining those properties would be misleading to the ordinary reader. I shall therefore term them "quantula" to avoid misleading connotations.

In FIG. 2 I have shown a preferred form of product wherein a carrier 10 has on its surface quantula 12 and 14, specifically different as regards the materials thereof. The dimensions marked thereon are typical. Outlines are diagrammatic only. The altitude (perpendicular to the plane of the paper viewing FIG. 2) will generally be less than two-thousandths of an inch. It will be helpful to observe that the end of a commonly used ballpoint pen, which is a stylus making a rather fine line of deposited ink, is of such width that it would span the entire group of quantula shown in this figure and engage all of them. In printer's measure the width of the group is about two points, and the area only about one-thirtieth that of one pica em quad. The entire group shown could be received within a square with sides one-sixteenth of an inch long with room to spare. In general the invention contemplates that several quantula of each kind will be received in such an area.

The megascopically uniform appearance of the coating may be understood by another analogy. It is well known that a half-tone picture is an assemblage of minute dots of ink in various densities of distribution in the various lights and shades of the picture. In a coarse half-tone in a newspaper even the unaided eye may apprehend that fact. In a better grade half-tone it may appear on inspection with a lower power magnifying glass. The attempt to discern details of the original object represented in a half-tone by use of a magnifier will usually be unsuccessful. We then see the trees but not the forest, the dots but not the outline of the object represented. In a superior half-tone the "solid" blacks of the original so appear to the naked eye in the reproduction. From a high flying airplane a green lawn, even a green forest, appears as a solid green surface.

The use of two numerals 12 and 14 in FIGS. 2, 4 and 5 and the contrasting lining on the areas so designated disclose that the coating comprises quantula of two different kinds (there will be at least two). The materials in the quantula 12 and 14 are reactants which on mixing give rise to a conspicuous difference in appearance in the area of mixing. The expression "reactants" usually will signify a reaction in the chemical or physico-chemical sense. The change in appearance will ordinarily be a difference in color and may be termed a "chromogenetic" reaction or change. The two kinds of quantula are present in co-substantial numbers, that is, they may not be equal in number for a given area, or collectively of equal area or equal volume or equal weight, but in these respects one will not be only a very small fraction of the other.

In FIG. 5 there are shown reactants applied in alternation as narrow longitudinal stripes or streaks (in fact hair like) along the carrier. In FIG. 4 these stripes become a series of dots. In a preferred form shown in FIG. 2, (one presenting decided advantages in manufacture as will appear) the quantula form a quincunx or staggered pattern the elements of adjacent vertical files being offset and desirably overlapping as shown. Herein the elements of each file carry the same reactant. However, if we draw lines at 45°, we perceive ranks and files with alternate elements different and a migration of material across the intervening air gaps initiated by a diagonal component of movement would be particularly effective in mixing the reactants.

Let us consider the effect of drawing a stylus as diagrammed in FIG. 1 with light pressure across a sheet as shown in FIG. 2. It should be borne in mind that the end of the stylus is broad relatively to the size of the quantula and the air gaps between them. An ordinary penpoint is as wide as the area delineated in FIG. 2. Here again an approach by analogy may be useful. If ink has been spattered on a desk and appears thereon as little separate drops, if we draw a small brush (a "pencil") across the area we will brush out a series of the droplets into a line. If we have thrown down shovelfuls of earth one after another in closely spaced relation along our garden bed, and then draw a rake along the row, the little mounds are merged and mixed. So the stylus merges and mixes the quantula in its path, causing at least one of the materials therein to move across the separating gaps which relatively isolate them and the materials react with a resultant conspicuous change of appearance which delineates the path and constitutes an inscription. If, in the case of spattered ink we had pressed down our thumb, we would have pushed together the droplets beneath it to produce a smudge of considerable area. Similarly if we press a raised type face on the inscription medium it will crush the quantula beneath it and push together the materials therein or permit their flow to mix with one another.

The quantula have previously been referred to as close one to another yet isolated. "Isolated" obviously means that there is such a space between adjacent ones that the reactant material in one will not influence that in another. The distance need not be great, a miss here is as good as a mile, but it is real. By "close" is meant that the intervening spaces should not be so wide, having regard to the volumes of materials involved and their physical state when the inscription is being made, as to prevent mixing by movement of material across the gaps. The distances involved are always small, although percentage-wise there might be considerable variation. Perhaps it could be said that the ideal would be to make the spaces as small as is consistent with effective isolation under the conditions of storage and handling. The dimensions marked on FIG. 2 by way of example represent one adequate approximation to this ideal and one susceptible of attainment by such procedures and mechanisms as later described.

While theoretically the chromogenetic or other reaction arising from the admixing of different quantula might be a solid phase reaction, a prompter and more pronounced effect will occur if one at least is liquid at the time of mixing. The occurrence of a reaction will of course be influenced by the "environment," the conditions of heat, pressure, humidity, etc., at the place of use and those due to the particular inscribing method used. Thus a heated stylus or a concentrated beam of radiant heat might melt one material or the mixture of two solids might melt more easily than either alone, and thus react. The reactions however would not strictly be solid phase reactions. In cases of recording measuring instruments where the inscription would be a curve showing the changes of a variable condition, the tracer moving responsively to such changes might release locally to the inscription medium some product of the process being observed which would be potent to initiate the reaction between adjacent quantula over which the tracer moved.

Since the dots are over the uninscribed medium there is no contrast and the megascopic impression would be one of uniformity. Psychologically it is recognized as an approximate rule of thumb that a series of 100 discrete dots to an inch represents the dividing point at which the average eye will no longer differentiate between discrete dots and a continuous line or 100 x 100 to the square inch, a continuous film. A substantially lower number will be apprehended as dots and a substantially higher number as a continuous line or surface. Provided the size and spacing of the dots are so related to

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the inscribing instrumentality as above explained, an inscription will be produced. For some applications a perceptible dot pattern in the inscription is acceptable, just as a medium screen half-tone might be. The closer spacing of a finer dot pattern would produce a better quality inscription.

Conveniently the material when viewed by the naked eye is substantially white, but may be of a suitable color. Thus in manifolding different colors for the different copies are desirable. This does not mean that some of the reactants in themselves or one array of quantula may not be dark colored. The analogy of textile fabrics, wherein a judicious mixture of white yarns with dark will give an overall gray effect without any conspicuous stripe or pattern, may be recalled. The fine subdivision involved also tends to make the appearance lighter than similar material in massy form.

A quantulum as 12 comprising a solid reactant may in certain cases be formulated by melting the reactant or dissolving it in a common solvent to produce a fluid or semi-fluid which may be "printed" onto the carrier much as ink is printed and which, when set, will adhere. Otherwise it may be produced by dispersing the material in very finely divided solid form in a fluid suspending medium, molten or a solution, quantula of which may be applied at proper spaced relationship to the carrier and dried, the continuous phase of the suspension medium then forming a binder securing the solid particles. The physical relationship of the components will be comparable to the suspension of solid pigments in a fluid in the case of a printing ink.

Liquid bearing quantula may be deposited as a dispersion of minute liquid droplets (marked 14a in FIG. 2) in a suspending medium. The fluid mixture will be an emulsion. The dispersion produced from such an emulsion by setting of the external phase is also sometimes termed an emulsion, but that usage is inexact. An encapsulating medium may be included which encloses each droplet in a shell and such a shell will persist in the dispersion. Rupture of the shell will release the liquid.

There has been discussed a system comprising two arrays of quantula, respectively of different material. Thus one set representing one material might be arrayed in rank and file and the other similarly arrayed, but with its elements out of register with those of the other, so that the elements of the two are interspersed, but individually each of the elements is isolated from all the others. Clearly there might be more than two arrays, say each different from both the others. The materials of three such arrays might be inert to one another pairwise, but when brought together all three give rise to a reaction useful for the purposes. Similarly in a two array system, two of such three materials might be in one array and the third in the other. One of the two materials might be a catalyst promoting the reaction between the others, or it might serve as a flux when the inscribing involves substantial added heat. In some cases the production of a gas might be the first stage following mixture and the gas enter into a secondary reaction to produce the significant change. The generation of a gas as a by-product of such a change, the gas simply being dissipated, would be unusual, but conceivable.

The inscribing medium should withstand reasonable handling. Thus it should not smudge by ordinary contact with the fingers or by the rolls of a typewriter if such a machine is used for inscribing. The contacts involved in those cases are over such relatively huge areas compared to the size of the quantula or the effective areas of a stylus point or a character of raised type. The product should also not deteriorate, become "fogged," if piled up in sheets or rolled up in successive convolutions. In other words it should have a good "shelf life." To ensure this it is preferred to make the solid phase quantula 12 of greater altitude than the more frangible liquid-bearing quantula 14 as illustrated diagrammatically in

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FIG. 3. Their tops will then take the pressure and contact with the tops of liquid-bearing quantula is avoided. The pressure here referred to is distributed over a large area and supported by multitudinous surfaces of the greater height. The difference in height may and should be small so that the stylus applied in a small area will not skip from one height to another and miss an intervening liquid-bearing quantulum of lower elevation.

It may be worth while to point out that the quantula would in practice probably not have so regular a form as is shown in diagrammatic FIGS. 2 and 3. They would be initially shaped by the mechanism used in applying them and forces of surface tension would tend to produce more or less spherical or ellipsoidal shapes. However an attempt to show shape in these figures would not be realistic either and the pretence is avoided.

For preparing the product described, suitably selected stencilling or printing techniques may be adopted and adapted. In general the quantula will be supplied in a fluid or semi-fluid state analogous to the inks in the conventional operations of the processes in question.

For small production runs or for testing purposes stencilling is available utilizing the methods and techniques of the "silk screen" process.

More generally the work may be performed by an intaglio printing press or a suitable modification thereof, no inks being used of course. The reactants are prepared as a fluid or semi-fluid form analogous in that property to ordinary inks and having due regard to the nature of the base sheet to which they are applied, and are handled in general as are ordinary inks.

By intaglio reference is made to a printing surface (plate or cylinder) in which are formed depressions corresponding to the design to be printed, which are filled with "ink" after which the original even surface is wiped clean. The surface is presented to the paper with light pressure and the ink is picked up by the paper from the depressions. The cylinders or plates of a press of this general type are usually operated so that the ink on the paper will spread beyond the area of the depression and merge with that of some adjacent depression. In the present instance that will not be the case.

While die-stamping and flat-bed printing from intaglio surfaces might be used, for economic reasons a rotary printing cylinder would probably be used commercially and the machine employed would be a multicouple, rotary, intaglio, sheet or web press. FIG. 6 is a diagrammatic representation of a web press.

The succeeding paragraphs are limited in expression to a two array system of quantula, each array being formed of individual quantula relatively spaced in a geometrical arrangement and the two combined with the elements in each relatively spaced from those in the other. Thus in FIG. 5 alternate vertical stripes constitute one array of parallel stripes and the intervening one the companion array, as indicated by the use of separate reference numerals 12 and 14. The reactants in the respective arrays are different. In FIG. 4 a series of separate small areas replaces each stripe and those of one kind constituting one array might be considered as arranged in rank and file, while those of the other array are likewise so arranged, but with the ranks and files offset relatively to those of the first array. In this particular arrangement, as has already been pointed out, there are diagonal extending rows alternate elements of which are diverse. The width of the two systems need not be the same. It is possible to have the solid array wider than the "liquid" dispersion array to support more of the total (storage) pressure of the weight of flat paper on paper.

In practicing the invention I may first imprint stripes 12 in the case of FIG. 5, or areas 12 in the case of FIGS. 2 and 4 and cause the impressions to dry or set and then, as by a second cylinder, imprint stripes 14 or areas 14 in the intervening spaces and in spaced relation to the former or, to use the printer's term, in proper "register,"

having in mind the result to be produced. Patterns of the desired delicacy and accuracy may be produced on the metal rolls by chemical etching, in particular by the procedure known as "inverted half-tone screening," or by mechanical engraving as on a jeweler's lathe. In chemical etching I prefer, but am not restricted, to the type of cell known as an "inverted half-tone," with less than 50% tone, i.e., with the cell walls not quite touching.

In general the array of quantula 12 which do not contain liquid should be printed first. If the liquid containing quantula were first printed they might be crushed by the smooth outer surface of the succeeding couple and the liquid would be released. This may seem inconsistent with the recommendation previously given that the solid ones be of greater altitude than the liquid-containing ones and it might be asked how the liquid-containing ones could reach the web. However the pressure of the second couple comes from a roll of elastic material and is exerted only in a narrow zone transverse of the path of the "paper." The solid deposits when set are of such compressibility and have such elastic recovery as to permit the liquid-containing ones, which are fluid when printed and may then be of greater depth when dry, to be subsequently applied to the paper without objectionable spreading or shortening of the previously applied solid ones.

In providing for accuracy of the register it is proper to consider variations in the area of the paper during the printing operation and variations in the functioning of the mechanical elements of the press.

FIG. 6 is a schematic representation of a form of rotary multi-couple intaglio press of the type such as might be used for preparing the product of the invention. In describing this I shall in the next paragraph use the word "ink" as the one most readily understood when the description relates to a press, but it will be understood that it really means the fluid or semi-fluid mixtures previously referred to which on drying form the potentially reactive quantula.

The web W is led from the left, as indicated by the arrow, from a suitable source of supply and through any conventional or suitable web conditioning means used in the art. Preferably it may be passed through a first non-printing couple comprising a hard surface, smooth roll 20 in size similar to the engraved rolls which will thereafter do the printing and moving at like speed, and a cooperating impression roll 22 similar to the impression roll of the following printing couples, the two rolls being urged together to provide the same pressure as those printing couples. The purpose of this couple will hereinafter be explained.

The web then advances to the first printing couple, comprising an engraved roll 24 taking ink from an inking supply 26 with which roll cooperates the doctor blade 28 which cleans off the surface of the roll, leaving the ink in the sunken portions, and the web then passes beneath the impression roll 30 whereby ink is transferred from the depressions of the etched roll to the paper. The web then continues over supporting rolls 32 opposite a drying mechanism 34 (schematically shown) to set the ink and then passes to a second couple like the one just described, past another dryer, and goes at the right of the figure to the rewinding or sheeting mechanism.

In good quality presses of this kind as presently manufactured it is possible to feed ordinary webs through under a substantially constant tension. It is possible to control the so-called side to side register along the web within very close limits, say half a thousandth of an inch. The control of fore and aft or "linear" registration is not so good more particularly because the diameters of successive cylinders can hardly be made exactly equal. The web is subject to dimensional changes due to changes in temperature, pressure and humidity. In the case of paper which has a decided grain, these changes are primarily longitudinal.

The control of the consistency of the "inks" and the

pressure of the couples is a matter within the skill of an able pressman.

The purpose of the first couple diagrammed is to apply initially to the web before printing the amount of pressure which it will encounter in passing through the printing couples, so that its area will be as invariable as possible during the succeeding printing operation.

By referring to FIG. 5 which shows the quantula applied in longitudinal streaks, the elements of the different areas alternating, and to FIGS. 2 and 4 wherein the quantula are arranged in rank and file and each "file" (vertical in the figures) is formed by quantula of the same composition, it is clear that unintended mixing of the quantula, due to inaccuracies in the printing process, will arise from variations in the side to side register, and therefore arrangements of this kind are recommended as this control is well within the capacity of precision gravure presses as presently known.

In the case of the streaked or striated form shown in FIG. 5, in practice, instead of having completely annular grooves etched in the printing cylinder, it may be convenient to interrupt them at intervals to provide shoulders cooperating with the doctor blade as the cylinder turns in such manner that excess material will be removed by the doctor blade, but only excess material, the grooves remaining full. These partitionings need not be aligned in adjacent grooves, and they may be fairly widely spaced. It will be seen, however, that if the stripes of FIG. 5 are interrupted at intervals the construction will tend to approach the construction of FIG. 4, although the individual deposits may be much longer lengthwise of the web.

A number of exemplary formulations follow.

Examples—Group I

In the preferred formulations, the solid phase is applied as a dispersion in a solvent-soluble binder, while the liquid dispersion is applied as an emulsion in a hot melt. In the following group of examples, the solid reactant consisted of 10 parts of brom-thymol blue ball milled in 100 parts of a solution of a film-forming binder containing 15 parts of resin and enough solvent to produce a viscosity of between 120 and 60 seconds, at 20° C., as measured by a No. 2 Zahn Cup, except for the screen printing operation, where the solvent was allowed to evaporate until the "ink" had a paste-like viscosity. The resin and solvent combinations were:

Dow Standard Ethylcellulose, 10 cps. (viscosity determined in an 80–20 toluene ethanol mixture), with the solvent medium toluene and isopropyl alcohol.

Rohm & Haas Acryloid B82 (a commercial name for a polymer of esters of acrylic and methacrylic acids) in toluene.

Nitrocellulose RS ½ second, a nitrocellulose ester made by Hercules Powder Co. Solvent toluene.

Note that the Ethocel has also been applied from isopropyl and butyl alcohol solutions. There is no limitation as to the nature of the solvent used except that set by the solubility of the binder. Where the solvents evaporate too fast (as in the case of a sheet-fed intaglio plate press) slower evaporating solvents such as xylene or butyl alcohol will be used, as is the custom in ink formulations. In general, I have not found it necessary to use a plasticizer in the binder, but conventional plasticizers can be used freely if a more flexible binder is wanted.

The alkaline, hot melt liquid reactant of the preceding example also reacts well with a solid reactant consisting of a ball-milled dispersion of

	Parts
Phenolphthalein	30
Ethyl cellulose	10
Toluene	106

This pair of reactants is colorless, and turns pink when the liquid is broken.

The "solid" reactants have all been applied as dispersions, prepared by ball milling the solid reagent in a solution of the resin (usually ball milled 16 hours), and then adjusting the viscosity of the dispersion to the desired "printing" viscosity. On a conventional gravure press the viscosity range of 60 to 120 seconds prints well—on an intaglio plate press, a viscosity of up to 180 seconds can be used.

The liquid dispersion was prepared by premelting together:

100 parts of Cumar V-1 (a coumarone-indene resin manufactured by the Barrett Division of Allied Chemical & Dye Corporation) having a softening point of 110° C. are melted together with 20 parts of U.S.P. white mineral oil, 0.5 part of Igepal CA-630 (a surface active agent of the nonionic alkyl phenoxy polyoxyethylene ethanol type, manufactured by Antara Chemical Division of General Dyestuff Corporation) and heated to 110° C. A separate solution of 27 parts anhydrous potassium carbonate was dissolved in 86 parts of ethylene glycol, heated to 120° C., and was dispersed in the hot coumarone-indene solution, using a high-speed turbine-type colloid mill to achieve good dispersion. The colloid mill is conveniently preheated to 120° C., in an oil bath. The emulsion or dispersion formed is of the water-in-oil type, i.e., the ethylene glycol droplets form a discontinuous phase completely surrounded by a continuous phase of the coumarone-indene resin. This dispersion is applied on a press at a temperature of 115°–120° C., using a heated plate or roll and a heated "ink fountain."

NOTE.—10 parts of calcium oleate may be used instead of the Igepal as a surface-active agent. Many other suitable surfactants are available.

The pairs of solid dispersions e.g., ball milled bromthymol blue in a binder and the hot-melt dispersion of alkaline ethylene glycol were applied to a 16 lb. white bond paper by five different procedures.

A. On an engraver's plate press, using a photo-engraved chrome-plated copper plate, engraved with a series of lines 0.0036 deep, 0.004 inch wide, separated 0.0135 on center. The solid dispersion was applied to the plate, wiped clean with a doctor blade, printed, and dried. The same engraver's plate was then moved over half the spacing of the lines (using registration pins); the plate (and the bed of the press) were heated to 120° C. (heaters are built right into the press), the hot-melt liquid dispersion was applied to the plate, the plate was wiped clean by a heated doctor blade, and the paper which had already been "printed" with the solid dispersion was reprinted with the hot-melt and was immediately cooled. The hot-melt lines were printed cleanly between the lines of the solid dispersion.

B. A conventional rotary-gravure press was used. The steel gravure printing roll was mechanically engraved on a lathe to have circumferential grooves 0.0135 inch apart on center, 0.0035 inch deep, and 0.0036 inch wide. This roll printed parallel lines in the direction the paper travelled. The solid reactant was printed first at room temperature, and was dried continuously in conventional fashion; the hot-melt liquid dispersion was then printed on a similar roll at 120° C. (the printing roll, ink fountain, and doctor blade were preheated to the desired temperature). The paper was moved over half the width of the line so that the melt-liquid registered between the dry dispersion. The melt was allowed to solidify at room temperature before the paper was rewound. The time for solidification is short enough so that it takes place in the space on the press usually used to dry inks. A chill roll is not needed, although it can be used.

C. The dispersions were run on the press exactly as in B, but the printing rolls were photo-engraved with an inverted half-tone pattern containing 85 dots to the inch,

at 30% tone (i.e., the dots or semi-spherical depressions covered 30% of the total roll surface), and a depth of 0.0055 inch at the center. While it was convenient to apply both reactants with rolls engraved the same way, it is equally practical to apply one component with a roll having a 40% tone and the second having a 30% or 45% tone, provided the spacing of the half-tone dots (center to center) is identical on the two rolls, when properly registered, by conventional gravure printing methods.

D. The dispersions were applied as in C, but the rolls were photo-engraved with an inverted half-tone dot pattern having 100 dots to the inch, at a 35% tone, 0.0045 inch deep. The paper was run through a printing station (i.e., with a blank smooth roll), and then through conventional driers; thereafter it was printed with the solid reactant and dried, and with the liquid reactant, at 120° C. and cooled. Because the dot pattern was so fine, registration had to be carried out with extreme accuracy, and the stabilization of the paper by the pre-printing operation was of help in maintaining the necessary registration.

E. A metal plate 0.006 inch thick was perforated by conventional photo-engraving techniques with a series of half-tone dots, forming an 85 line screen, at 35% tone. This screen was mounted in a conventional "silk-screen" press, and the dry-reactant was screened on paper by forcing the "ink" through the holes in the screen by a conventional squeegee, in the usual stencil (silk-screen) printing operation. After the prints were dry, the screen and a special synthetic polymer squeegee were preheated to 85° C. and the hot-melt dispersion was applied at 85° C. (instead of 110° C.). This temperature was selected because it produced a viscosity of the melt that was suitable for screen printing.

In all the above examples, the printed sheet had an orange-yellow color. When it was marked with a stylus, pencil or typewriter, or a letterpress print, a bright blue mark was formed immediately.

The same solid and liquid reagents have been applied to 20-lb. bond paper, to newsprint, to super-calendered white paper. As in all printing the rate of operation of the press, the pressure of the back-up roll, and the viscosity of the reagent "inks" had to be adjusted to suit the stock being printed just as these adjustments have to be made in conventional ink printing operations.

For commercial production I prefer in general to apply our reagents by procedure B because this procedure yields the minimum difficulties with registration (only lateral registration is needed). The roll need not be mechanically engraved. I have used equally well similar rolls engraved with rows of conventional gravure cells (i.e., rectangular in shape) and with rows of so-called inverted half-tone shape. I prefer the latter type of cell, because it can be readily engraved in steel or magnesium-faced rolls which can be chrome plated or, in the case of the magnesium, anodized, to yield a very long printing life.

Examples—Group II

In this group both the solid and the liquid are applied in a volatile solvent medium of the type used in conventional gravure printing. In the following group of examples the solid reactant (ferric sulfate) was applied as a ball milled dispersion in the concentrations of

	i, parts	ii, parts
Ferric Sulfate.....	60	80
Dow Ethoel 10 cps.....	20	20
Toluene.....	165	192

(to produce a viscosity of 60 seconds at 20° C., as measured by a No. 2 Zahn Cup). Again, conventional plasticizers may be used if wanted.

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The following liquid reactants were applied:

A	Parts
Parlon S-5 (a chlorinated rubber manufactured by Hercules Powder Co. having a viscosity of 4-7 centipoises at 25° C. in a concentration of 20% in toluene) -----	35
Diphenylphthalate (other conventional plasticizers may be used) -----	5
Toluene -----	60
Igepal CA-630 -----	0.5
Into this solution is dispersed a solution of	
Ethylene glycol -----	75
Water -----	25
Gallic acid -----	16

A turbine-type or similar colloid mill is used to attain a stable water-in-oil emulsion.

B	Parts
Cumar V-1 (as in Group I examples) -----	35
Diphenylphthalate -----	5
Dow Ethylcellulose, Standard type, 168 cps. viscosity -----	2
Igepal CA-630 -----	0.5
Toluene -----	60
into which are dispersed, with a colloid mill, a solution of	
Ethylene glycol -----	133
Water -----	131
Gallic acid -----	32
NaOH -----	3.3

This dispersion is thixotropic—it is fluid enough to print effectively when feeding from the colloid mill and may be rendered fluid again subsequently by active agitation. The presence of the alkali makes the reaction somewhat more effective than without the alkali. Other alkalies may also be used; the highly hygroscopic nature of the sodium hydroxide however is of assistance in retaining equilibrium moisture in the printed dispersions.

C	Parts
Gum damar -----	62.5
Toluene -----	62.5
Igepal CA-630 -----	0.5
into this solution was dispersed a solution of	
Ethylene glycol -----	76
Water -----	30
Gallic acid -----	19

This next example illustrates a different binder.

D	Parts
Parlon S-5 -----	35
Diphenylphthalate -----	5
Toluene -----	60
Igepal CA-630 -----	0.5

NOTE.—Other surface-active agents can be used instead the Igepal CA-630. It is one which is effective.

Into this solution was dispersed a separate solution of

	Parts
Gelatin (195 Bloom, 51.5 viscosity) -----	8.1
Water -----	96.5
Ethylene glycol -----	85.4
Gallic acid -----	32

The presence of the gelatin keeps the printed dispersion moist. The same formulation without the gelatin did not remain effective for as long a time as it did with the gelatin. Gelatin can be incorporated in all the other formulations (including hot-melt formulations containing no water but only ethylene glycol) to increase the viscosity

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of the liquid phase and to assist in forming a good dispersion.

These reagents were applied in pairs (one solid reagent, one liquid) by the procedures described under B and C of Example I, except that in this group the liquid reagent was applied at room temperature, like a conventional ink, not as a hot melt, and was dried after printing in the conventional manner.

The paper containing these reactants marked with various types of styli and on a typewriter operated without a ribbon, to yield a black to brownish-black reactant.

Examples—Group III

The solid reactant was applied as a ball milled dispersion of

Potassium ferrocyanide -----	90
Ethocel, 10 cps -----	20
Toluene to make a viscosity of 90 seconds at 20° C.	
as measured by a No. 2 Zahn Cup.	

The liquid dispersion consisted of

A	Parts
Parlon S-5 -----	35
Diphenylphthalate -----	5
Igepal CA-630 -----	0.5
Toluene -----	60
in which was dispersed a solution of	
Ferric ammonium sulfate -----	50
Ethylene glycol -----	120
Water -----	80
i.e., a solvent-type "ink." This was applied on the press at room temperature.	

B	Parts
Cumar V-1 -----	100
Dibutyl phthalate -----	10
U.S.P. white mineral oil -----	0.5
Melted together and cooled to 95°C. then dispersed into it was a hot (95° C.) solution of	
Ferric ammonium sulfate -----	20
Ethylene glycol -----	48
Water -----	32
i.e., a hot-melt; this melt was applied at 95° C. on the press.	

Both of these combinations were applied by procedures B and C of Example I, to yield effective record papers that were white in color and gave a black record trace.

Examples—Group IV

In Example I if we substitute for the hot-melt (cumar example given) the following:

example given) the following:	Parts
55 Carnauba wax -----	20
Gum dammar -----	80
Igepal CA-630 -----	0.5
Ethylene glycol -----	86
60 Potassium carbonate -----	27

we have a reactant that does not work with pressure, but does work when melted with a hot stylus.

I need hardly point out that the above examples are merely illustrative. My invention does not reside in having used the cited reactants or any other of the many reactants reported in the patent and technical literature. Any of the well-known reactions may be applied by my process to yield a working product. Whereas in the prior art multiple layers of the reactants are piled upon each other, with the well-known drawback of such products, by my process the reactants are kept safely apart but still sufficiently close to react when the liquid dispersion is broken by an activating stylus, typewriter key or letter-

press type.

It is of course possible to have both reactants applied as liquid dispersions in binders instead of having one reactant solid. In general however it will be obviously better from an economic and practical point of view to have as many components as possible applied as solids.

The multiplicity of binders used in making printing inks can all be effectively used in practicing the invention. It will be evident that the selection of such a binder will be made first because of the surface on which it is to be printed, second because of the solvent to be used, and finally from a cost standpoint. Certainly so far as solid reactants are concerned practically every known binder that is flexible enough for the intended base on which it is to be printed will be adequate for use. In general the weight of binder used will range from twice the weight of reactant to one-tenth the weight of the reactant. Any conventional plasticizers may be used with these binders. The solid reactant may be applied as a hot-melt instead of solution. The necessary change in the formulations to achieve any desired type of binder are well known in the ink and coating arts. The spreading of the "ink" with the particular printing equipment and web used should not permit the two reactants to merge during the printing operation. Since this factor varies with the particular press and paper used, it is not practical to specify numerically here the exact formulation that should be used in any given application. It will be well within the skill of any ink maker to establish a suitable formulation in order to produce liquid reactants in a binder that will not spread on any particular specified web.

So far as the liquid reactants are concerned, the primary requirement is that the binder be readily broken by the inscribing instrumentality and that the reactant be effectively encapsulated by the binder until it is broken by pressure or by heat.

I am aware that the invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof, and I therefore desire the present embodiment to be considered in all respects as illustrative and not restrictive, as is in fact clear in several matters from the description itself. Reference is to be had to the appended claims to indicate those principles of the invention exemplified by the particular embodiment described and which I desire to secure by Letters Patent.

I claim:

1. The method of making an inscription medium which comprises imprinting on a base with a fluid formulation of a first potentially reactive material a two-dimensional array of closely arranged but effectively isolated impressions, drying the same to set the impressions, then printing in the interstices between the impressions, with a fluid formulation of a second potentially reactive material which if mixed with the first results in a chromogenetic reaction, a second two dimensional array of impressions closely arranged with but effectively isolated from both each other and the impressions of the first array and drying the second impressions, the density of distribution of the elements of the two arrays taken together being such that at least several of each array are present in any area one sixteenth of an inch square.

2. The method of claim 1 wherein the elements of each array form longitudinal files.

3. The method as set forth in claim 1 wherein the elements of the first group of impressions are solid when set and those of the second comprise liquid droplets dispersed in a binder.

4. The method as set forth in claim 3 wherein the impressions of the first group are of such volume that they are of greater altitude than those of the second group when both are dried.

5. A material for receiving inscriptions which material is of megascopically homogeneous surface texture and tone and comprises a base sheet having individually adherent to the surface thereof the elements of several two-dimensional arrays, each of regularly arranged and rela-

tively spaced small masses containing at least one potentially reactant material, which reactant materials of the masses of the several arrays, if mixed, will initiate a reaction resulting in a conspicuous change in appearance, the elements of the arrays respectively being out of register each with each of the others and the elements of each array, and of all the arrays considered as one, being spaced from one another on the surface of the base sheet, the individual areas and density of distribution of such elements being such that at least several of each kind are present in any area of the sheet one sixteenth of an inch square, the masses being distortable under the influence of an inscribing instrumentality presented to and moving relatively to the material along or transversely to its surface so that the material of the masses of one array overruns spaces which normally isolate them to mix operatively with the adjacent masses of other arrays to effect localized reaction between the reactant materials with the resultant appearance of a conspicuous inscription.

6. A material as set forth in claim 5 wherein the masses of one array contain two ingredients, inert to each other, but one of which promotes the reaction of the other with the different potentially reactive ingredient in the masses of another array when the masses of the two arrays are mixed.

7. A material as set forth in claim 5 wherein the masses of at least one array are formulated from liquid droplets dispersed in a binder.

8. A material as set forth in claim 7 wherein the masses of another array are formulated in solid form and are of greater altitude than the masses which contain liquid droplets.

9. A material as set forth in claim 7 wherein the masses of one array are formulated as a dispersion of fine solid particles of potentially reactive substance in a binder and the masses of another array are formulated as a dispersion in a binder of fine liquid droplets of a substance reactive with the last mentioned reactive substance.

10. A material for receiving inscriptions which material is of megascopically homogeneous surface texture and tone and comprises a base sheet having individually adherent to the surface thereof the elements of a first two-dimensional array of regularly arranged and relatively spaced small masses containing at least one potentially reactant material and a second two-dimensional array of regularly arranged and relatively spaced small masses containing at least one potentially reactant material which if mixed with reactant material of the masses in the first array will initiate a reaction resulting in a conspicuous change in appearance, the elements of the two arrays respectively being out of register and the elements of each array, and of the two arrays considered as one, being spaced from one another on the surface of the base sheet, the individual areas and density of distribution of such elements being such that at least several of each kind are present in any area of the sheet one sixteenth of an inch square, the masses being distortable under the influence of an inscribing instrumentality presented to and moving relatively to the material along or transversely to its surface so that the material of the masses of one array overruns spaces which normally isolate them to mix operatively with the adjacent masses of the other array to effect localized reaction between the reactant materials with the resultant appearance of a conspicuous inscription.

References Cited in the file of this patent

UNITED STATES PATENTS

137,775	Jameson	Apr. 15, 1873
595,281	Yetter	Dec. 7, 1897
1,778,397	Maier et al.	Oct. 14, 1930
2,224,270	Sanders	Dec. 10, 1940
2,618,573	Green	Nov. 18, 1952
2,655,453	Sandberg	Oct. 13, 1953
2,730,457	Green et al.	Jan. 10, 1956