

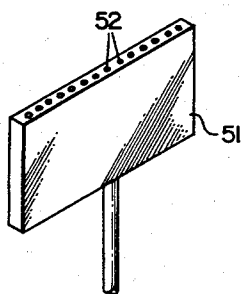
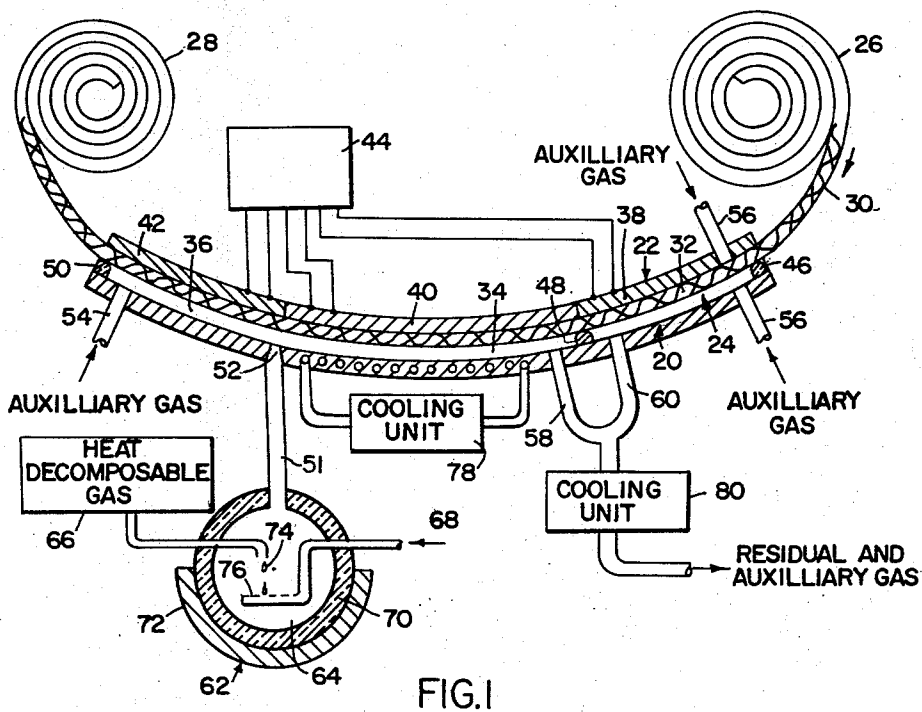
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VAPOR DEPOSITION

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VAPOR DEPOSITION

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1 Claim. (Cl. 118—48)

The present invention relates to the deposition of metal on sheet material and, more particularly, to the deposition of metal from a gaseous compound of which the metal is a component. Although the device of the present invention is applicable to a variety of organic and inorganic sheet materials, it is particularly useful for coating paper. In the coating of paper, many of a variety of requirements must be met. Thus, in the production of metal coated decorative paper, deposition must be effected rapidly and inexpensively. And in the production of metal coated capacitor paper, deposition must be precisely controlled to meet specific characteristics. In all cases, temperature, pressure and time must be selected carefully in order to avoid scorching and outgassing of the paper and to ensure adherence and uniformity of the metal coat.

The primary object of the present invention is to provide a novel device by which a metal is deposited. The heat decomposable metal compound may be normally solid or liquid but must be vaporizable without undue decomposition. The device is characterized by an elongated convex surface in contact with which the elongated sheet is tensioned and which defines, in conjunction with an associated elongated concave surface, a curved chamber for subjecting the elongated sheet to the metal bearing vapor in a novel manner. The process involves the steps of heating the elongated sheet, which specifically is composed of paper, and depositing on one of its faces a metal from its vapor in a predetermined sequence that results in an adherent coat of high quality. The system and process effect the decomposition substantially at atmospheric pressure.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the apparatus involving the several steps and components and the relation and order of one or more such components with respect to each of the others, which are exemplified in the following disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description, taken in connection with the accompanying drawings, wherein:

FIG. 1 is an exaggerated cross-sectional diagrammatic view, partly broken away, of a device for performing a process in accordance with the present invention; and

FIG. 2 is a perspective view of a component of the device of FIG. 1.

The specific process performed by the device of FIGS. 1 and 2 involves the steps of advancing an elongated sheet of paper from a supply spool through a curved path to a take-up spool, the path being defined by a heated convex

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surface against which the sheet is tensioned and a cooled concave surface which is slightly spaced from the sheet. The sheet is tensioned against the convex surface to prevent the back of the paper as well as the convex surface from being affected by the deposition process. The sheet is spaced from the concave surface and the concave surface is cooled to provide a region within which the metal bearing gas may flow in contact with the surface of the sheet to be coated and to prevent deposition from occurring on the concave surface in such a way as to constrict this region. The metal bearing vapor is flowed through an entrance port into a deposition zone of the region and through an exit port from the deposition zone. Auxiliary gas is flowed into zones on opposite sides of the deposition zone in order to isolate the metal bearing vapor and its residue from the extremities of the region into which and from which the sheet advances. In this system, the metal bearing compound is an organometallic, a metal hydride, a metal carbonyl or a metal halide, which may be heated in the presence of a suitable auxiliary gas, to an elevated temperature at which decomposition of the vapor and deposition of the metal occurs. It is known that useful rates of metal deposition from such gaseous metal bearing compounds occur generally within the range of from 200° to 1000° F. It has been found that paper can withstand, without appreciable physical-chemical change, temperatures within the range from 1 to 100 seconds, a typical paper being able to withstand without appreciable chemical change a temperature of approximately 500° F. for approximately 30 seconds. In the illustrated process, successive increments of a paper sheet are heated and subjected to a metal bearing gas to cause metal to be reduced thereupon from a metal bearing gas. The auxiliary gas may be an active material such as hydrogen or an inert material such as argon (or other noble gas) or nitrogen. The overall pressure in evaporation chamber 64 preferably ranges from .1 to 15 p.s.i. above atmospheric pressure in order to concentrate the heat decomposable gas prior to its entrance into decomposition zone 34. Also, this pressure prevents the outgassed vapors from the paper from entering the decomposition zone.

Particularly good papers for the purpose of the present invention are calendered papers having at least a glossy surface at which the sheet is denser than it is in its interior.

The metal bearing compounds to be vaporized preferably are selected from carbonyls such as iron carbonyl, molybdenum carbonyl, nickel carbonyl, chromium carbonyl, tungsten carbonyl and cobalt carbonyl; alkyls such as aluminum diisobutyl hydride, aluminum triisobutyl, aluminum triethyl and molybdenum ditoluene; aryls such as chromium dibenzene, molybdenum dibenzene, vanadium dibenzene and vanadium dimesitylene di-iodide; sandwich compounds such as bis-cyclopentadienyls of iron, manganese, cobalt, nickel, rhodium and vanadium; esters such as cupric acetylacetonate, manganic acetylacetonate, titanyl acetylacetonate, platinum acetylacetonate, nickel acetylacetonate, dibutyl tin diformate, copper formate, cuprous formate and cuprous acetate; nitro compounds such as iron nitrosyl and cobalt nitrosyl carbonyl; hydrides such as antimony hydride, copper hydride, aluminum hydride, and tin hydride; and combinations and mixtures thereof such as alkyl and aryl carbonyls including benzene chromium tricarbonyl, phenanthrene

chromium tricarbonyl, naphthalene chromium tricarbonyl, o-xylene chromium tricarbonyl, benzene molybdenum tricarbonyl, cyclo-octadiene molybdenum tricarbonyl; bis-cyclopentadienyl chlorides, bromides and diiodides of titanium, zirconium, hafnium, vanadium, molybdenum, tungsten and tantalum, cyclopentadienyl carbonyls such as cyclopentadienyl manganese tricarbonyl, bis-cyclopentadienyl carbonyls of molybdenum, tungsten or iron, carbonyl halogens such as sodium carbonyl bromide, ruthenium carbonyl chloride, and organo hydride compounds such as triethyl amine-aluminum hydride and trimethyl amine-aluminum hydride.

The device illustrated in FIGS. 1 and 2 for performing the process of the present invention is shown generally as comprising an inwardly concave wall 20 and an outwardly concave wall 22 which define therebetween a curved chamber 24, the profile of which constitutes what may be termed a relatively minor segment of a closed curve. Preferably the distance between the adjacent surfaces of walls 20 and 22 ranges between $\frac{1}{32}$ and $\frac{5}{32}$ of an inch and preferably is approximately $\frac{1}{8}$ of an inch. Side walls (not shown) complete curved chamber 24 except for its ends. The open ends of chamber 24 are adjacent, respectively, to a supply spool 26 and a take-up spool 28 for a substrate 30 to be advanced through chamber 24. Chamber 24 includes a preheat zone 32, a decomposition zone 34 and a dwell zone 36. Substrate 30 advances through preheat zone 32, decomposition zone 34 and dwell zone 36, in sequence, while constrained against wall 22 throughout its length. Wall 22 includes sections 38, 40 and 42, which respectively incorporate separate heating elements, extending throughout their lengths, that are energized by a suitable electrical source 44.

Gaskets 46, 48 and 50 respectively, partially seal zone 32 from its exterior, zones 32 and 34 from each other and zone 36 from its exterior. A mixture of auxiliary and heat decomposable gas is introduced at the junction of zones 36 and 34 through a series of small holes in a vent component 51, one hole of which is shown in FIG. 1 at 52. Additionally, auxiliary gas is introduced at the outer extremities 54 and 56 of zones 36 and 32. Residual and auxiliary gas is exhausted from zones 34 and 36 at the junction 58 between zone 34 and zone 32. Auxiliary gas is exhausted from zone 32 at its inner extremity 60. The arrangement is such that heat decomposable gas is directed only through decomposition zone 34 in consequence of higher pressures of the auxiliary gas in preheat zone 32 and dwell zone 36.

The source of the heat decomposable gas-auxiliary gas mixture is shown at 62 as including a vessel 64 into which the heat decomposable gas and the auxiliary gas are introduced from suitable sources 66 and 68, a water jacket 70 for distributing heat throughout the exterior of vessel 64, and a heating unit 72 for water jacket 70. In the illustration, the heat decomposable gas is supplied in liquid form as successive drops 74 and is vaporized by a series of jets 76. It will be noted also that the concave surface of zone 34 is cooled as at 78 in order to prevent deposition thereupon and that the gas exhausted at the junction of zones 32 and 34 is cooled as at 80 in order to increase the exhaust effect. In general, the temperatures generated in preheating zone 32 and dwell zone 36 are below the decomposition temperature of the decomposable gas and the temperature generated in decomposition zone 34 is above the decomposition temperature of the decomposable gas.

EXAMPLE I

A paper substrate was advanced through chamber 24 of FIG. 1 at 15 ft./mm. Heating section 38 was at 160° C., heating section 40 was at 235° C. and heating section 42 was at 190° C. The spacing between the adjacent curved surfaces of chamber 34 was $\frac{1}{8}$ inch. Water jacket 70 was at 85° C. The partial vapor pressure of iron pentacarbonyl was 100 mm. Hg, the total vapor pressure within

chamber 64 was 10 oz. per sq. inch. The remaining nitrogen was introduced at slightly greater than atmospheric pressure in order to ensure outward flow through the extremities of chamber 24. The flow of gas through decomposition chamber 34 is at the rate of 5 cu. ft./hr. a coat, 5000 A. thick, composed of 98.5% iron and 1.9% carbon resulted.

EXAMPLE II

The process of Example I was repeated except that the substrate was paper coated with casein. A ferromagnetic stratum was deposited on the casein coating.

EXAMPLE III

The process of Example I was repeated except that the substrate was Mylar. A ferromagnetic stratum was deposited.

EXAMPLE IV

The process of Example I is repeated except that nickel carbonyl and cobalt carbonyl in 2 to 1 ratio, respectively, and in a quantity equal to $\frac{1}{2}$ the vapor pressure of the iron carbonyl is introduced into the system. The resulting product includes a coating of approximately 59% iron, 24% cobalt, 14% nickel and 3% carbon.

EXAMPLE V

The process of Example IV is repeated except that a partial pressure of copper hydride and aluminum triisobutyl in 2 to 1 ratio with respect to each other and in amount approximately equal to the vapor pressure of the nickel is introduced. The resulting product is composed of approximately 49% iron, 24% cobalt, 14% nickel, 8% aluminum, 3% copper and 1% carbon.

Preferred ferromagnetic strata of the above described character are produced in the system of FIG. 1 where: the heat decomposable gas is an iron carbonyl, preferably iron pentacarbonyl, which is liquid under usual conditions; alternatively the iron carbonyl may be iron dodecacarbonyl; the auxiliary gas is an inert gas such as nitrogen; the temperature of heating section 38 ranges from 140–180° C.; the temperature of heating section 40 ranges from 160–250° C.; the partial pressure of the heat decomposable gas ranges from 75 to 125 mm. Hg; the auxiliary gas is supplied in such a way as to produce a flow through decomposition chamber 34 ranging from 1 to 10 cu. ft./hr.; and substrate 30 is advanced at a rate 1–80 ft./min.

Accordingly, the present invention provides novel systems for producing thin metallic coats of high quality. Since certain changes may be made in the foregoing description and the accompanying drawing without departing from the scope of the invention herein involved, it is intended that all matter disclosed herewith be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

An apparatus for depositing metal on an elongated sheet material, said apparatus comprising first means providing an outer concave surface and second means providing an inner concave surface, said outer concave surface and said inner concave surface being spaced apart a distance ranging from $\frac{1}{32}$ to $\frac{5}{32}$ inch and defining a concave path said path providing in sequence a preheat zone, a decomposition zone and a dwell zone, means for advancing an elongated sheet material through said concave path and tensioned against said inner concave surface, means for heating said inner concave surface substantially continuously throughout said decomposition zone, means for cooling said outer concave surface substantially continuously throughout said decomposition zone, means defining an entrance port and a first exit port at opposite extremities of said decomposition zone, means for directing a heat decomposable metal bearing gas through said entrance port, said decomposition zone and said first exit port, means for directing an auxiliary gas into said preheat zone and said dwell zone in order to

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shield the outer extremities of said preheat zone and said dwell zone from said heat decomposable gas, a first gasket at the outer extremity of said preheat zone, a second gasket at the junction between said preheat zone and said decomposition zone and a third gasket at the outer extremity of said dwell zone, means defining a second exit port in said preheat zone, said first exit port and said second exit port being contiguously located on opposite sides of said second gasket, and means for exhausting said first exit port and said second exit port, the profile of said concave path being such that it constitutes a relatively minor segment of a closed curve.

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