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VAPOR DEPOSITION DEVICE

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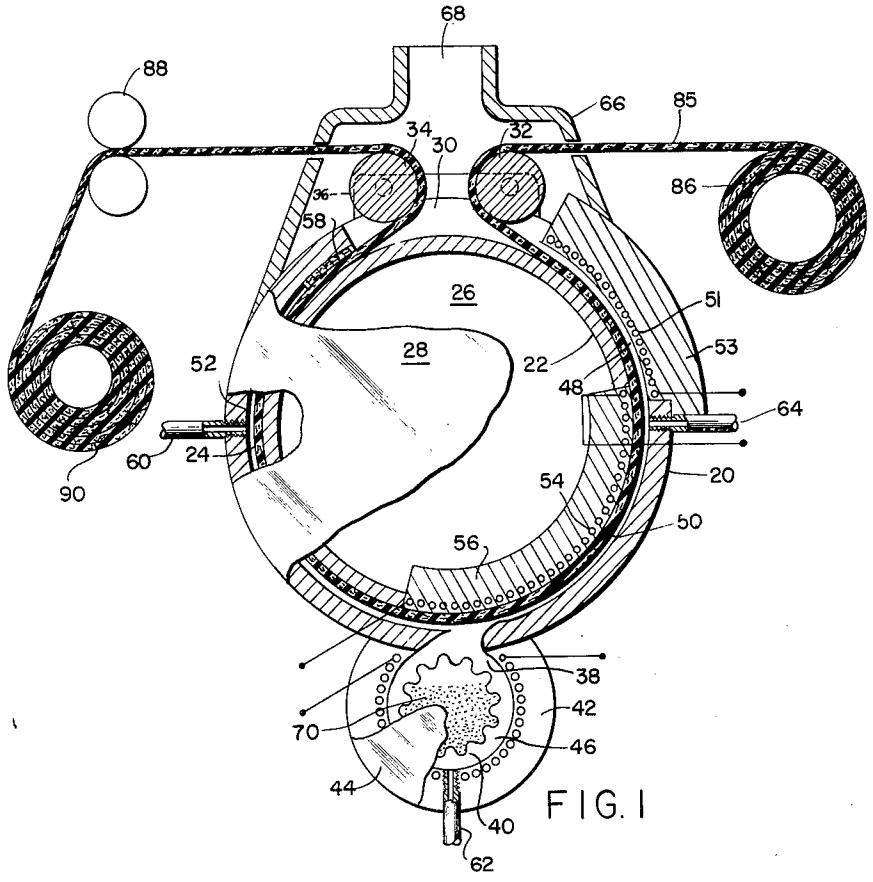


FIG. 1

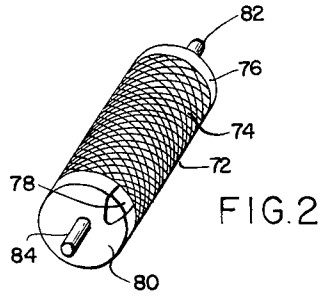


FIG. 2

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VAPOR DEPOSITION DEVICE

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The present invention relates to the deposition of metal on sheet material and, more particularly, to the deposition of metal onto paper from a gaseous compound of which the metal is a component. 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 carefuly in order to avoil scorching and outgasing 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 may be deposited onto an elongated sheet from a gaseous metal bearing compound under precisely controlled conditions of temperature, pressure and time. The device is characterized by a drum around which the elongated sheet is tensioned and which defines, in conjunction with an associated jacket, an annular 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.

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 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 a 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 one of a pair of adjacent rollers through an annular path to the other of the pair of adjacent rollers, the path being defined by the outer surface of a drum and the inner surface of a casing. The annular path in profile may be thought of as extending throughout almost the whole extent of a closed curve. The sheet is tensioned against the outer surface of the drum to prevent the back of the paper from being affected by the deposition process. A part of the outer surface of the drum is heated so that heat is transmitted from the rear face of the sheet to its front face at which metal deposition is to occur. The inner face of the casing is provided with an opening, adjacent to which is a rotary cage containing the metal bearing compound from which the metal bearing vapor is to be formed. The metal bearing vapor is formed by flowing an auxiliary gas through this cage and the resulting mixture of metal bearing vapor and auxiliary gas is

directed through the opening into the annular path. 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 of 200° to 1000° F. for periods 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 momentarily 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. Although the heated gas mixture is applied in a limited zone, it is free to diffuse rapidly into other zones of the annular path. The overall pressure in this zone preferably ranges from .1 to 15 p.s.i. in order to prevent outgassing of the paper.

Particularly good papers for the purposes 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. Such a paper is sold by S. D. Warren under the trademark Lusterwrap.

The gaseous metal bearing compounds preferably are selected from: carbonyls such as ferric carbonyl, molybdenum carbonyl, nickel carbonyl, chromium carbonyl, tungsten carbonyl and cobalt carbonyl; alkyls such as aluminum diisobutyl, aluminum triisobutyl, aluminum triethyl and molybdenum ditoluene; aryls such as chromium dibenzene, molybdenum dibenzene, vanadium dibenzene and vanadium dimesitylene di-iodide; olefins such as biscyclopentadienyls 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 and copper acetate; nitro compounds such as copper 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, phenathrene chromium tricarbonyl, naphthalene chromium tricarbonyl, o-xylene chromium tricarbonyl, benzene molybdenum tricarbonyl, cyclo-octadiene molybdenum tricarbonyl; biscyclopentadienyl chlorides, bromides and diodides 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 aluminum diethyl hydride and aluminum dimethyl hydride.

The device illustrated in FIGS. 1 and 2 for performing the process of the present invention is shown generally as comprising an outer jacket **20** and an inner drum **22** which define therebetween an annular chamber **24**. Preferably the distance between the outer surface of drum **22** and the inner surface jacket **20** ranges between $\frac{1}{32}$ and $\frac{1}{4}$ of an inch and preferably is approximately $\frac{1}{8}$ of an inch. A rear panel **26** and a front panel **28**, both of which are connected to edges of jacket **20** and drum **22**, complete the enclosure of chamber **24** as well as the hollow interior of drum **22**. Jacket **20** is open at a restricted upper section **30**, which is adjacent to a pair

of rolls 32, 34. These rolls are journaled at their opposite extremities on a suitable frame, shown in part at 36, which is connected to rear panel 26. Jacket 20 is open at a restricted lower section 38. Communicating with chamber 24 through open lower section 38 is a vaporizing chamber 40, which is defined by a casing 42. Casing 42 is connected to jacket 20 at open lower section 38. The front and rear faces of chamber 40 are enclosed by front and rear panels 44 and 46.

Chamber 24 may be thought of as comprising a preheating zone 48, a metal plating zone 50 and a cooling zone 52. The temperature of preheating zone 48 is controlled by a suitable electrical resistance filament 51, which is adjacent to the inner surface of jacket 20 and embedded in a suitable electrical insulator and heat conductor 53. The temperature of metal plating zone 50 is controlled in temperature by a suitable electrical resistance filament 54 which is adjacent to the inner surface of drum 22 and embedded in a suitable electrical insulator and heat conductor 56. Cooling zone 52 is bounded at its outer free extremity by a fibrous seal 58, the outer surface of which is resiliently urged by the seal itself toward the outer surface of drum 22 in such a way that while the elongated paper sheet advances between the seal and the drum, cooling zone 52 remains sealed from opening 30. Inlet ports for the auxiliary gas are provided to cooling zone 52 at 60, to vaporizing chamber 40 at 62 and to preheating zone 48 at 64. The arrangement of these inlet ports is such that auxiliary gas flows readily from cooling zone 52 into plating zone 50 and auxiliary gas mixed with metal bearing vapor flows from vaporizing chamber 40 into plating zone 50. The resulting gaseous mixture flows from plating zone 50 through preheating zone 48 and opening 30 from chamber 24. The result is to preclude the entry of air through opening 30 into chamber 24.

The result is enhanced by a hood 66, which covers opening 30 and associated rollers 32 and 34 which provides another opening 68 through which exhaustion occurs. It will be observed that the metal bearing compound, shown in granular form at 70 within chamber 40, is enclosed within a cage 72 (FIG. 2). Cage 72 includes a medial tube composed of a screen 74. At one end of screen 74 is a solid cap 76. At the other end of screen 74 is a solid rim 78, which is mated with a solid removable cap 80. Extending oppositely from caps 76 and 80 are a pair of stub shafts 82 and 84. The arrangement is such that as auxiliary gas is introduced through inlet port 62, cage 72 rotates in order to continually present, to the stream of gas through inlet 62, fresh surfaces of the granular compound within cage 72.

In operation, an elongated sheet of paper 85 is advanced from a supply spool 86 through a slot in housing 66 around roller 32 and into contact with drum 22, while in contact with drum 22 the paper is advanced through preheating zone 48 within which it is heated from its exposed surface, through metal plating zone 50, within which it is heated through its rear face, and through cooling zone 52. From cooling zone 52 the elongated sheet is advanced between seal 58 and the contiguous surface of drum 22 around roller 34, through a pair of drive rollers 88 and to a takeup spool 90. During advancement of the elongated sheet in the forward direction, auxiliary gas and metal bearing vapor are directed through chamber 24 in the reverse direction.

The following non-limiting examples will further illustrate the present invention:

Example I

In one specific example of the foregoing process effected by the above described apparatus, an elongated paper sheet of the type having a glossy calendered surface sold by S. D. Warren under the trademark Lusterwrap is advanced into contact with drum 22 and with its glossy face remote from drum 22. Nitrogen, heated

to approximately 90° C., is introduced through ports 60, 62 and 64. In consequence of the passage of nitrogen through rotating cage 72, the vapor of molybdenum carbonyl, heated to approximately 90° C., is introduced into plating zone 50. The partial pressure of the nitrogen is approximately five times the partial pressure of the molybdenum carbonyl. The total pressure throughout chamber 24 is approximately 50 mm./mg. Filaments 51 and 56 both generate a decomposition temperature of approximately 250° C. The flow rate through the plating chamber is approximately .5 cubic foot per hour. When the paper is advanced at a rate of 2 inches per minute a molybdenum layer approximately .001 inch thick results.

Example II

The foregoing process is repeated except that the auxiliary gas is nitrogen and the metal bearing gas is chromium dicumene.

Example III

The process of Example I is repeated except that the auxiliary gas is nitrogen and the metal bearing gas is iron dodecacarbonyl, the decomposition temperature being 135° C.

Example IV

Example I is repeated except that the inert gas is argon and the metal bearing gas is cyclo-octadiene molybdenum tricarbonyl, the decomposition temperature being approximately 110° C.

Example V

The process of Example I is repeated except that the auxiliary gas is hydrogen and the metal bearing gas is copper acetylacetonate, the decomposition temperature being approximately 300° C.

Example VI

The process of Example I is repeated except that the auxiliary gas is hydrogen and the metal bearing gas is aluminum hydride, the decomposition temperature being 100° C.

Since certain changes may be made in the above apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. An apparatus for depositing metal on an elongated sheet material, said apparatus comprising a housing including an inner cylindrical drum and an outer cylindrical casing, the inner surface of said casing and the outer surface of said drum being spaced apart a distance within the range from 1/32 to 1/4 inch and defining an annular passage, said casing having an opening at a first position of said passage for permitting said elongated sheet material to enter said passage at a first extremity thereof and to leave said passage at a second extremity thereof, said first extremity and said second extremity being adjacent to each other, said casing having an opening at a second position of said passage, a first auxiliary casing communicating with said opening at said second position, a rotatable cage within said first auxiliary casing, a conduit for introducing an auxiliary gas into said first auxiliary casing for flowing said auxiliary gas through said cage and acquiring a heat decomposable metal bearing vapor from granular material in said cage, a second auxiliary casing communicating with said opening at said first position for exhausting said passage, first heating means for heating the inner surface of said casing at said first extremity of said passage, second means for heating the outer surface of said drum at said first position, and conduits for introducing auxiliary gas through said casing between said entrance and said first position and between said exit and said second position, said annular

passage in profile extending throughout almost the whole extent of a closed curve.

2. An apparatus for depositing metal on an elongated sheet material, said apparatus comprising first means providing an outer tubular surface and second means providing an inner tubular surface, said outer tubular surface and said inner tubular surface being spaced apart a distance ranging from 1/32 to 1/4 inch and defining an annular chamber, said outer surface being provided with a first opening in a first section thereof, said outer surface being provided with a second opening in a second section thereof, means for advancing an elongated sheet material through said annular chamber and tensioned against said first surface, means for heating a section of said first surface and inlet means to said chamber for the introduction of an auxiliary gas and a metal bearing vapor, sealing means in said annular chamber for causing flow in a direction counter to the travel of said elongated sheet material, annular chamber in profile, extending throughout almost the whole extent of a closed curve.

3. The apparatus of claim 2 wherein said inlet means includes a rotary porous cage at said second opening for retaining a quantity of metal bearing compound for generating said metal bearing vapor.

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