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VAPOR DEPOSITION PROCESS

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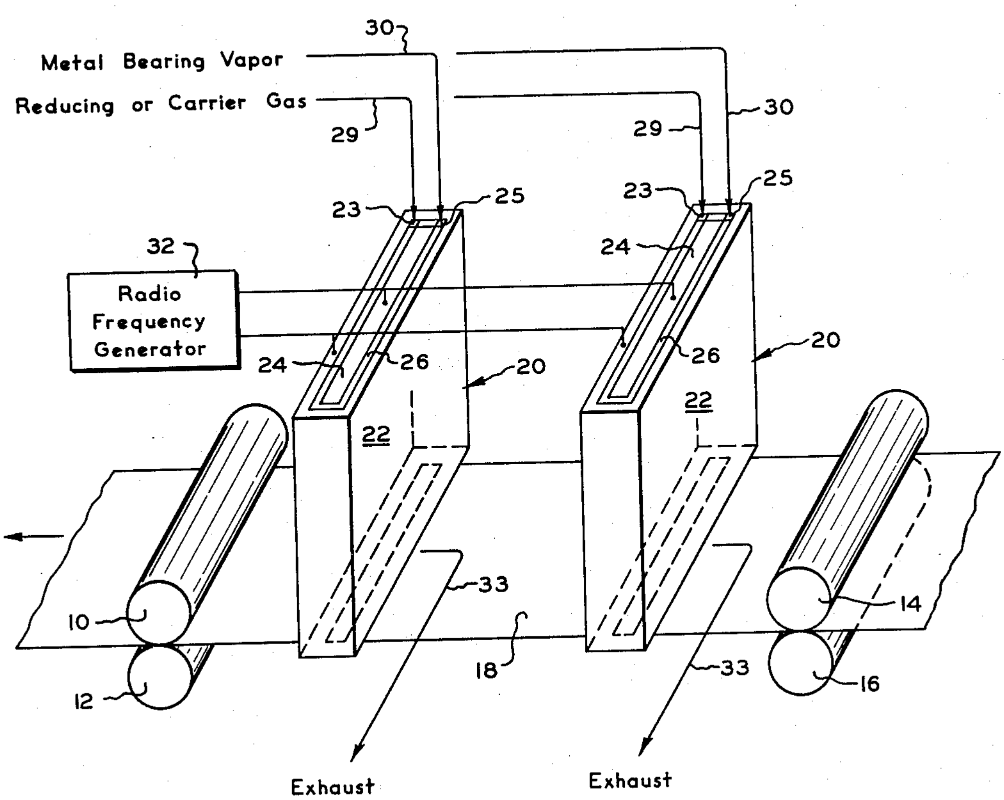

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VAPOR DEPOSITION PROCESS

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The present invention relates to the deposition of metal, particularly on such a sheet material as paper, and, more particularly, to the deposition of metal from gaseous compounds of which the metal is a component. In the coating of paper, for example, any 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 requirements. In all cases, temperature, pressure and time must be selected critically in order to avoid scorching and outgasing of the paper sheet and to ensure adherence and uniformity of the metal coat.

Primary objects of the present invention are to provide novel processes by which a metal bearing gas is subjected to electromagnetic energy of a microwave or a radio frequency such that the metal may be deposited while the gas is at relatively low temperature. This process is such that a metal may be deposited from a gaseous metal bearing compound under precisely controlled conditions of temperature, pressure and time, and such that paper may be coated with a metal so deposited under temperature conditions which do not alter its physical-chemical properties.

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

The invention accordingly comprises the process involving the several steps and relations and order of one or more of such steps 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 drawing, wherein there is illustrated diagrammatically a length of paper undergoing a process of the present invention.

Generally the process specifically illustrated herein comprises coating an elongated paper sheet by exposing successive increments thereof to a radio frequency excited gaseous metal-bearing compound at a temperature at which metal may be produced from the compound and for a period during which significant change in the physical-chemical composition of the paper does not occur. In a typical system the metal-bearing compound is a halide which may be reacted with hydrogen in order to produce the metal or an organometallic which may be heated to an elevated temperature at which it decomposes in order to reduce the metal. 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 of from 1 to 100 seconds, a typical paper being able to withstand without appreciable physical-chemical change a temperature of approximately 500° F. for approximately 30 seconds. In the illustrated process, the applied radio frequency energy lowers the temperature at which a feasible rate of metal deposition occurs to a temperature below that at which a feasible

rate of metal deposition normally occurs. Preferably, a narrow coherent frequency band is selected to produce resonance in the metal bearing gas molecules so that energy transfer of high efficiency results. The term "coherent" is used herein in the accepted physics sense to designate what in theory may be thought of as a single wavelength and in practice actually is a narrow wavelength or frequency range. "Coherent" is contradistinguished from "non-coherent" which refers to radiation of widely dispersed wavelengths or frequencies, for example, black body radiation. Such radiation ranges from 1 to 10 megacycles per second and from 3000 to 100,000 megacycles per second in frequency and upward from 250 watts in power. This radiation is applied either in continuous or pulsed form. This radio frequency energy is imparted by a waveguide or other microwave (or radio frequency antenna system) through which the intermixed metal bearing gas and an auxiliary reducing or carrier gas flow. A typical reducing gas is an active material such as hydrogen and a typical carrier gas is an inert material such as argon. The waveguide acts as a nozzle to focus the heated metal bearing and auxiliary gas mixture upon the exposed surface of the paper sheet so that primarily the outer portions of the sheet only are subjected to heating and the inner portions of the sheet are protected therefrom. Although the heated gas mixture is applied in a limited zone, it is free to diffuse rapidly into other regions of a larger compartment in which the zone is located. The overall pressure is this zone preferably ranges from .1 to 20 p.s.i. in order to prevent outgasing of the paper.

The paper sheet to be coated in accordance with the illustrated process generally is composed of matted cellulose fibers. In conventional fashion, the fibers may be produced, for example, by the sulfite process in which chipped wood is treated with a solution of calcium bisulfite, the soda process in which chipped wood is treated with a solution of sodium hydroxide or the sulfate process in which chipped wood is treated with a solution of sodium sulfite. The effect of such reagents is to dissolve the lignin of the wood and to leave as a residue substantially pure cellulose pulp. This pulp, after being bleached with chlorine, is converted into paper by suspending it in water, mixing it with filling and sizing materials and casting it on a moving support.

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; halides such as chromium chloride, tungsten chloride, molybdenum chloride, aluminum chloride, aluminum bromide, aluminum iodide, zirconium chloride, zirconium bromide, zirconium iodide, cobalt bromide, cobalt chloride, ferric chloride, germanium bromide, germanium chloride, manganese fluoride, molybdenum fluoride, tungsten fluoride, chromium fluoride, nickel bromide, nickel chloride, tin bromide, tin chloride, tin fluoride and titanium chloride; alkyls such as aluminum triisobutyl and aluminum triethyl; aryls such as chromium dibenzene, molybdenum dibenzene, vanadium dibenzene and vanadium di-mesitylene di-iodide; olefins such as bis-cyclopentadienyls of iron, manganese, cobalt, nickel, rhodium and vanadium; esters such as cupric acetylacetonate, manganic acetylacetonate, titanyl acetylacetonate, platinum acetylacetonate, copper formate and copper acetate; nitre compounds such as copper nitroxyl and cobalt nitrosyl carbonyl; hydrides such as antimony hydride and tin hydride; and combinations thereof such as, bis-cyclopentadienyl chlorides, bromides and iodides 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 apparatus illustrated in the drawing comprises two pairs of rollers **10**, **12** and **14**, **16** for advancing an elongated sheet of paper **18** through a hermetically sealed compartment. Contiguous with the path of paper **18** are a plurality of nozzles **20**, each in the form of a hollow waveguide having a rectangular tube portion **22** and an end probe portion **24** separated from each other by a suitable dielectric **26**. Ports **23** and **25**, at the outer end of wave guide **20** direct a mixture of metal bearing and reducing or carrier gas **29**, **30** toward an increment of paper **18**. The arrangement is such that the mixture normally in stable condition at the selected temperature is rendered unstable by the application of microwave excitation from a radio frequency generator **32**. In consequence metal from vapor **29** is deposited on the surface of paper **18**. Exhaustion occurs as at **33** by a suitable pump (not shown).

The following non-limiting examples further illustrate the present invention.

Example I

In a specific example of the following process, an elongated sheet of kraft paper is advanced through the above described apparatus. The vapor of molybdenum carbonyl is mixed by waveguide **20** with hydrogen at approximately five times the pressure of the molybdenum carbonyl and at a temperature of 100–150° C. Coherent energy of the order of 10 megacycles per second in frequency and 300 watts in power applied to waveguide **20**. The vapor deposition chamber is at atmospheric pressure and the combined flow rate through waveguide **20** is estimated at 500 ml./min. Under these conditions paper moving at a speed of approximately 3 inches per minute is provided with an adherent coat of molybdenum.

Example II

In another example of the foregoing process, an elongated sheet of kraft paper is passed through the above described apparatus. The argon, and the aluminum triisobutyl in 10 to 1 ratio and at a temperature of 300° F. are introduced through waveguide **20** excited at an energy of the order of 5000 megacycles per second in frequency and 300 watts in power. Exhaustion occurs from the chamber in order to cause a total flow rate of 500 ml./min. At a paper speed of approximately 3 inches per minute, an adherent coat of aluminum is produced.

Since certain changes may be made in the above processes and devices without departing from the scope of the invention herein involved, it is intended that all matter 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. A coating process comprising the steps of directing a stream of gaseous heat decomposable metal compound in a first path, said heat decomposable metal compound being selected from the class consisting of the metal halides, metal hydrides and organometallics, advancing a sheet of paper in a second path, said first path and said second path being contiguous at a given region, said region ranging in temperature from 200 to 1000° F., each increment of said paper moving at a speed by which it is in said given region for a period ranging from 1 to 100 seconds, the pressure within said given region ranging from .1 to 20 pounds per square inch, and energizing said stream with electromagnetic energy of frequency ranging from 1 to 10 megacycles per second and from 3,000 to 100,000 megacycles per second, said heat decomposable metal compound being characterized by a given resonant frequency, said electromagnetic energy being coherent and corresponding substantially in frequency to said given resonant frequency.

2. The coating process of claim 1 wherein said heat decomposable metal compound is molybdenum carbonyl.

3. The process of claim 1 wherein said heat decomposable compound is aluminum triisobutyl.

4. A coating process comprising the steps of directing a stream of aluminum triisobutyl and an inert gas in a stream along a first path said aluminum triisobutyl and said inert gas having an approximate ratio of 10 to 1 by total weight, advancing a sheet of paper in a second path, said first path and said second path being contiguous at a given region, the temperature of said given region being approximately 300° F. and the flow rate of said aluminum triisobutyl and said inert gas through said first path being approximately 500 millimeters per minute, the speed of said paper being approximately 3 inches per minute, said first path being defined by a wave guide, and energizing said wave guide at a frequency of approximately 5000 megacycles per second.

References Cited in the file of this patent

UNITED STATES PATENTS

2,698,812	Schladitz	Jan. 4, 1955
2,707,688	Blackman	May 3, 1955
2,865,790	Baer	Dec. 23, 1958