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P. J. CLOUGH ET AL
PROCESS FOR VAPOR COATING

2,665,224

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2 Sheets-Sheet 1

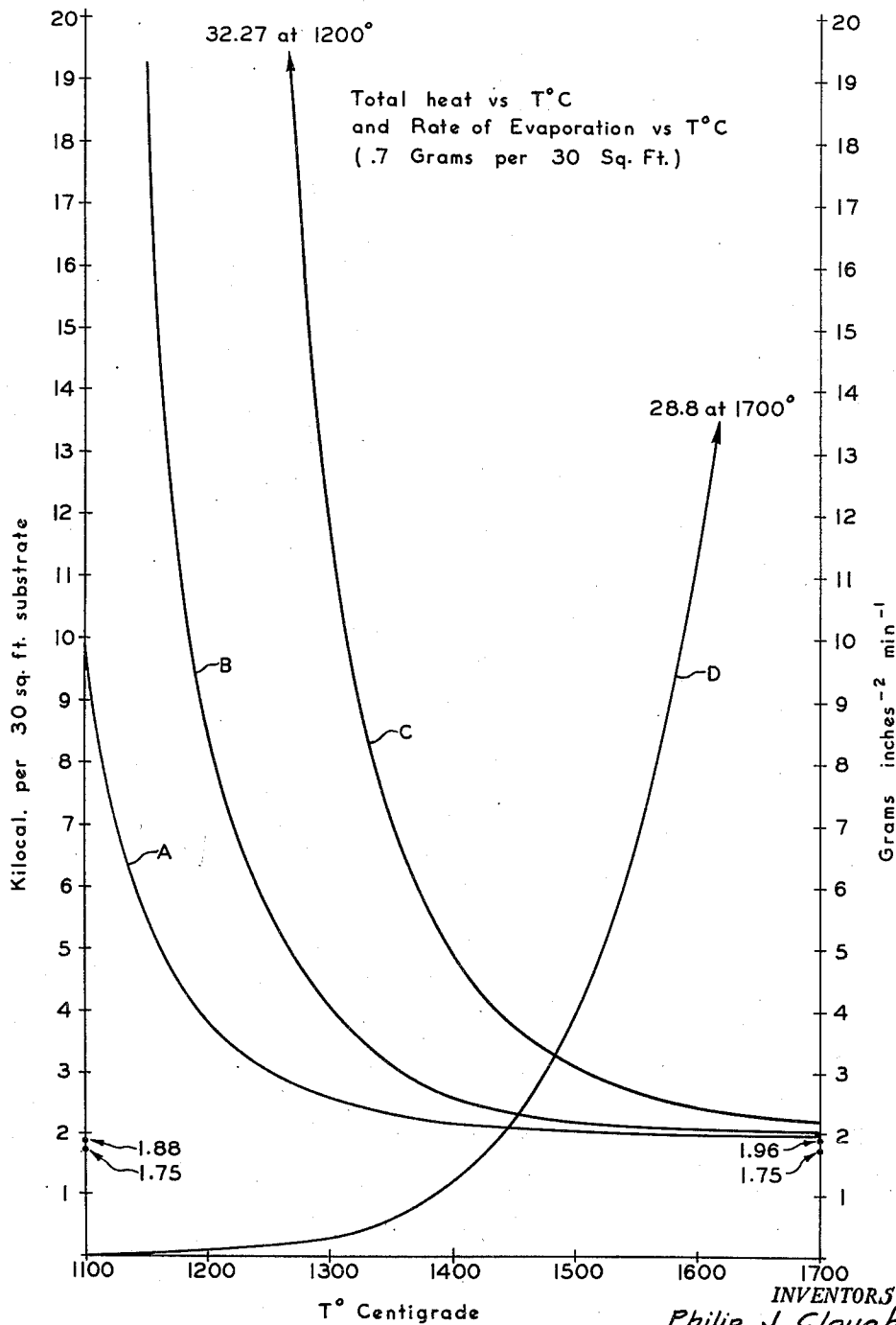


FIG. 1

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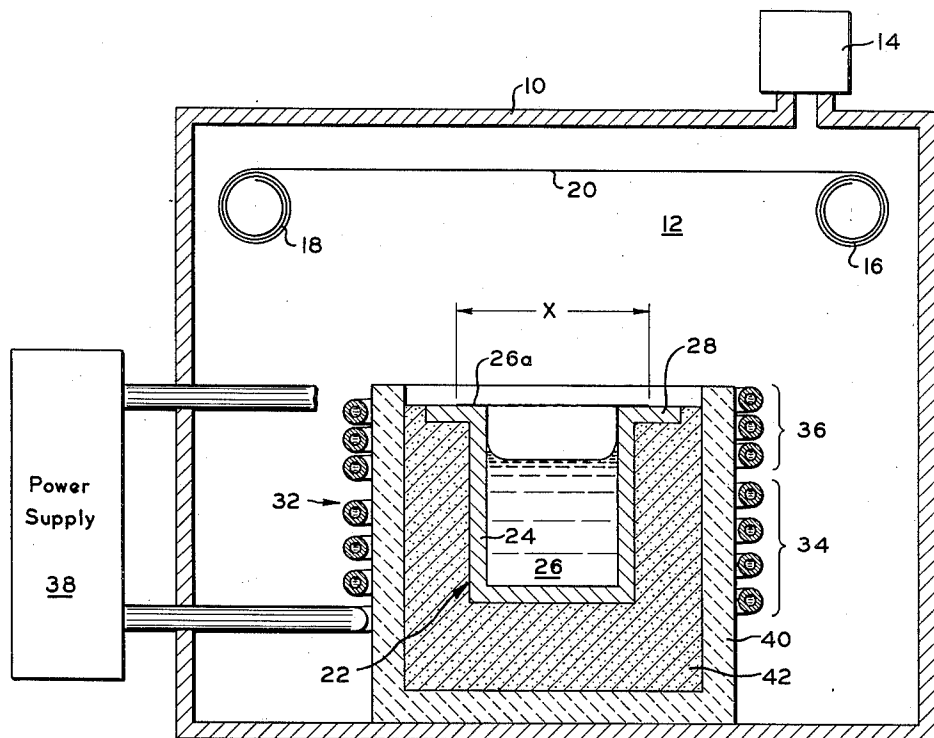


FIG. 2

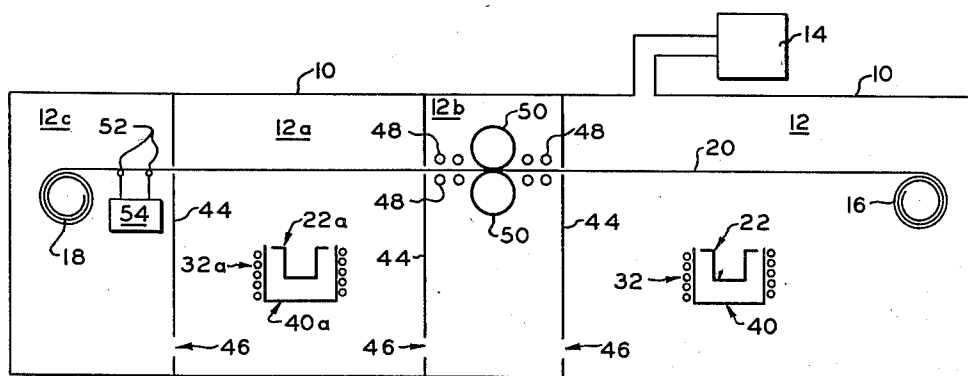


FIG. 3

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PROCESS FOR VAPOR COATING

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Application March 7, 1950, Serial No. 148,224

4 Claims. (Cl. 117-107)

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This invention relates to coating and more particularly to novel processes for coating a heat-sensitive substrate, such as paper, plastic, or the like, by vapor deposition of aluminum in a vacuum on such a substrate. This application is a continuation-in-part of the copending application of Earl E. Chadsey, Jr., et al., Serial No. 117,124, filed September 22, 1949.

In coating materials, such as paper, plastic, or the like, in a vacuum by vaporizing aluminum, the aluminum is evaporated by heating to a temperature such that the vapor pressure of the aluminum appreciably exceeds the residual pressure in the system. The aluminum vapor is then condensed on the substrate, forming a coat thereon. In this operation heat is transferred from the source of the aluminum vapors to the substrate. This heat is very serious in the case of heat-sensitive materials. The heating of the surface of the substrate in severe cases can cause a chemical change. Probably the greatest difficulty, however, arises from local outgassing of the surface due to the high temperature to which the substrate is subjected as a result of the coating. This local outgassing has the effect of spoiling the aluminum coat by providing poor adhesion and nonuniformity of coating. The resultant film coated on the outgassing substrate is not shiny, and it is apt to have a bluish tint rather than the silvery-white color desired.

In the prior art the local outgassing of such a heat-sensitive substrate has been prevented to a certain extent by attempting to outgas the substrate prior to the coating operation. This necessitates heating the substrate in a vacuum, a step which is itself apt to damage the substrate. Additionally, the apparatus necessary for carrying out such outgassing operations is relatively expensive and unduly increases the capital equipment costs necessary for coating such heat-sensitive substrates.

Accordingly, it is a principal object of this invention to provide a novel vacuum coating process which is capable of operating at high coating speeds with a minimum of outgassing equipment.

Another object of the invention is to provide a coating process of the above type which involves the use of a minimum amount of capital equipment for each unit area of substrate to be coated.

Still another object of the invention is to provide a process for coating heat-sensitive substrates without damage thereto.

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

The invention accordingly comprises the proc-

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ess involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

Fig. 1 is a graph showing the degree of transfer of heat to the substrate as a function of temperature and the quantity of vapor emitted from the source as a function of temperature;

Fig. 2 is a schematic, diagrammatic, partially sectional view of one preferred form of apparatus embodying the present invention; and

Fig. 3 is a schematic, diagrammatic, partially sectional view of a modification of the apparatus of Fig. 2.

The heat that is transferred to the substrate during vapor deposition coating reaches the substrate in three separate components. These are the heat liberated by the vapor condensing to the solid state, the heat liberated by the aluminum cooling to the temperature of the substrate, and the radiant heat from the source of the aluminum vapors.

The heat of condensation has been found to be essentially constant, within certain limits, if the temperature of the substrate is maintained near some definite value. The heat liberated when cooling the vapor is small compared to the heat of condensation, and the change in this heat, caused by the change in the temperature of the vapors, may be considered to be negligible. However, the heat transferred by radiation is not constant, but is a definite function of the temperature of the source.

It has been discovered that, for any given coating thickness, as the temperature of the aluminum from which the vapors emanate is raised, the total heat reaching a unit area of the substrate decreases. This is due to the fact that the rate at which the aluminum evaporates increases faster with increases of temperature of the source than does the rate at which the radiant heat is transferred. It has been found that, when the sum of the heat liberated by the vapors condensing to a solid state, and the heat liberated by cooling the vapors is greater than the radiant heat reaching the substrate due to increasing temperature of the source, the total heat reaching the substrate is such that outgassing becomes of mi-

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nor importance. In the practice of the present invention, therefore, the temperature of the aluminum is maintained above the temperature at which the heat carried to the substrate by the vapors is equal to the radiant heat.

Since the radiant heat from all sources reaching the substrate will increase as the temperature of these sources increases, it is essential, at least at temperatures below about 1400° C., to maintain those sources of radiant heat, other than the molten aluminum, as small as possible. It has been found in practice that this condition is satisfied when the effective area from which the aluminum evaporates is at least as great as the total of the other areas effectively radiating heat to the substrate.

Referring now to Fig. 1 there is shown a number of curves which illustrate the various conditions under which the present invention is operated. In Fig. 1 curves A, B, and C show the relationship between the total heat reaching 30 sq. ft. of the substrate as a function of the temperature of the aluminum vapors leaving the vapor source. Curve A is plotted on the basis of the molten aluminum surface constituting the sole source of radiant heat, while curve B is plotted on the basis of the molten aluminum surface being half of the source of the radiant heat with the other half of the source of radiant heat being carbon (of the crucible) at the same temperature as the aluminum. Curve C is similar to curve B except that the molten aluminum constitutes only $\frac{1}{4}$ of the total heat-radiating area. These curves are calculated on the basis of depositing .7 gram of aluminum per 30 sq. ft. of substrate, the coating efficiency being considered at 70%. These curves are also calculated on the basis that only 39% of the radiant heat reaching the substrate is absorbed thereby, the remainder of the radiant heat being reflected by the aluminum film forming on the substrate. The coating thickness depends upon the use for which the coated substrate is intended. Where the substrate is essentially smooth and the coated film is to have a high reflectance (i. e. above 90% of visible light) it is preferred to condense about .7 gram (94% reflectance) of aluminum on each 30 sq. ft. of substrate. In the calculation of the data from which these curves are derived, the emissivity of aluminum has been assumed to be $0.2 + (T^{\circ}\text{C.} - 1000) \times 10^{-4}$ while the emissivity of carbon has been assumed to be 0.526.

At 1100° C. the heat carried to the substrate by the vapors is indicated at 1.88 kilocalories/30 sq. ft., 175 of this being attributable to heat of condensation, and the remainder being heat of cooling the vapors. At the higher temperatures the heat of cooling the vapors increases somewhat and the heat carried to the substrate by the vapors rises to 1.96 kilocalories, the heat of condensation remaining the same.

Curve D shows the rate of evaporation of aluminum in grams per square inch of evaporating surface per minute as a function of the temperature of the aluminum.

From an examination of the various curves in Fig. 1, it can be seen that the lower temperature limit of operation of the aluminum vapor source is dependent upon (a) the coating thickness, (b) the degree to which the particular substrate material is damaged by heating or outgassing during coating, and (c) the ratio of area of the aluminum surface to the hot crucible surface area. In most cases it has been found that greatly improved coating results are achieved

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when the total heat absorbed by the substrate is on the order of, or less than, twice the heat carried to the substrate by the vapors.

When the molten aluminum is the sole source of radiant heat (curve A) the preferred lower limit of operation under the present invention approximates 1200° C. However, since it is extremely difficult to achieve a source where only the aluminum radiates heat to the substrate, in normal coating procedures practiced in accordance with the present invention, the conditions of operation fall near curve B, preferably between curves A and B. In this case the lower temperature limit occurs around 1300° C.

The upper temperature limit is determined by two factors: (a) the power that can be put into the aluminum vapor source, and (b) the degree to which variations in vapor emission can be tolerated or compensated for during coating, these variations of aluminum vapor emission arising from variations of the temperature of the aluminum vapor source. From an examination of curve D it can be seen that the rate of emission of aluminum vapors increases only moderately between 1200° and 1400° C. Between 1400° and 1500° C. the increase becomes quite substantial, and between 1500° C. and 1600° C. the rate increases very rapidly. Above 1600° C. the increase in vapor emission rate per degree increase in temperature is so great as to require extremely complex temperature and substrate speed controls. When solid aluminum is fed to the crucible, it will greatly vary the surface temperature of the molten aluminum, and consequently cause enormous variations in the vapor emission which are practically impossible to compensate for by variations in substrate speed. This is particularly true where the substrate is relatively delicate and cannot be subjected to the strains often necessary to achieve rapid changes in speed.

It should also be pointed out that the power in KW per square inch of evaporating aluminum surface greatly increases at the higher temperatures. A graph showing the power in KW per square inch of aluminum surface plotted against temperature follows curve D almost exactly. Consequently, in the practice of the present invention the upper limit of the aluminum temperature is chosen at about 1600° C. This limit, in a preferred form of the invention, is about 1500° C. since at 1500° C. the power requirements and the aluminum vapor emission rate are sufficiently low as not to require an unduly complicated apparatus.

Referring now to Fig. 2, there is shown one preferred embodiment of the invention wherein 10 represents a vacuum-tight housing providing a vacuum chamber 12, this chamber being kept at a pressure in the micron range by means of a vacuum pump system schematically indicated at 14. Within the chamber 12 there is provided a means for supporting a substrate to be coated, this means being shown schematically as a first spool 16 and a second spool 18 carrying therebetween the substrate 20.

The means for vaporizing the metal comprises a metal-holding crucible 22 having a main body portion 24, in which the metal 25 is to be held in molten condition and heated to a temperature sufficient to vaporize the metal at a high rate under the pressure existing in the vacuum chamber 12. Extending from the top of the main body portion 24, there is provided a lip 28 which is preferably formed integrally with the body por-

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tion 24. For providing heat to the metal 26 and the metal-holding crucible 22, there is included a heating means, schematically indicated at 32. This heating means preferably comprises an induction coil having a portion 34 for heating the main body of the crucible and the metal carried thereby, and a portion 36 for heating the lip 28 of the metal-holding crucible. A suitable power supply 38 is provided for furnishing a high frequency current to the induction coil 34, 36. The induction coil 34, 36 is preferably a water-cooled coil, such as a copper tubing, through the interior of which water is adapted to be circulated. As can be seen from Fig. 2, the turns in portion 36 of the coil, adjacent the lip 28, are closer together than the turns in portion 34 of the coil, adjacent the main body portion of the crucible.

For preventing radiation heat loss from the crucible 22, there is provided an outer crucible 40, preferably made of a refractory material which does not conduct electricity, and a refractory packing 42 between the metal-holding crucible 22 and the outer refractory crucible 40. Means for feeding metal to the crucible are also preferably provided but not illustrated. Such means may comprise a wire-feeding mechanism which feeds wire to the crucible at a rate equal to the rate of evaporation of the aluminum. Equally, the pellet-feeding mechanism described in the application of Earl E. Chadsey, Jr., Serial No. 130,453, filed December 1, 1949, may be employed for feeding aluminum to the crucible.

In a preferred form of the invention, the metal-holding crucible 22 is preferably formed of a current-conducting material, such as carbon or a graphite-carbon mixture of the type commercially available under the trade name "Graphitar." The graphite-carbon mixture preferably has an apparent density of about 1.65, and the crucible preferably includes a zirconium carbide inner skin. This skin may be formed by adding zirconium to the melt, or by applying a zirconia slurry to the inner surface of the crucible prior to melting the aluminum. This zirconium carbide skin is particularly effective in preventing the formation of aluminum carbide during the evaporation of the aluminum. The outer crucible 40 preferably comprises a refractory material, such as silica, while the refractory packing 42 preferably comprises zirconia or beryllia. The induction coil is preferably provided with a suitable source of high frequency current of approximately 10,000 to 500,000 cycles per second from a usual high frequency power source. When a "Graphitar" crucible 22 is employed for vaporizing aluminum, the resistivity of the charge (including the crucible) is about 1000. With such a charge and a frequency of about 100,000 cycles, the skin depth of the induced current is approximately 0.2 inch at the temperature employed. The wall of the crucible is thus preferably made slightly thinner than 0.2 inch so that some of the induced current flows in the molten aluminum charge.

In the use of the invention, illustrated in Fig. 2, a quantity of aluminum 26 is provided in the crucible 22 in the form of powder, rod, pellets, or the like. Chamber 12 is evacuated by the pump 14 to about 0.2 micron pressure, and power is supplied to the induction coils 34, 36. The amount of aluminum supplied to the crucible 22 is preferably high enough to fill the crucible to within a quarter of an inch or a half an inch from the top thereof. The molten aluminum tends to creep up the walls of the crucible and over the top sur-

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face of the lip 28 thereof. This creeping meniscus of molten aluminum is indicated at 26a.

While the aluminum is being melted in the body portion 24 of crucible 22, the lip 28 is also being heated by eddy currents induced therein from the top coil portion 36. As mentioned previously, there is a closer electromagnetic coupling between the coil portion 36 and lip 28 than there is between coil portion 34 and the crucible body 24. This is due both to the fact that the lip 28 extends outwardly towards the coil 36, and to the fact that the spacing between the turns in coil portion 36 is less than the spacing between the turns in coil portion 34. By means of this arrangement, lip 28 has a greater heat input thereto and will remain at a higher temperature than the temperature of the molten aluminum 26 in the body portion 24 of the crucible.

The molten aluminum, which creeps into contact with the hot lip 28, is evaporated more rapidly than the aluminum which is being evaporated from the main body of molten aluminum. This evaporation of the aluminum in contact with the lip 28 is maintained sufficiently high so that none of the aluminum is allowed to creep beyond the outer edge of the lip 28, the molten aluminum starting across the top of lip 28 being completely evaporated before it can reach the outer edge.

The lip 28 thus acts as a wick for increasing the evaporation area. The effective aluminum-evaporating area is thus the area indicated by the diameter X, rather than the area at the top of the pool 26 of molten aluminum in the crucible. From the approximate dimensions schematically indicated in Fig. 2, it can be seen that the effective aluminum-evaporating area of the aluminum is slightly larger than that portion of the area of the lip 28, which does not evaporate aluminum but does radiate heat to the substrate. However, since the lip 28 is hotter than the molten pool 26, the total heat reaching the substrate falls approximately on curve B. It can also be seen that the radiant heat leaving that portion of the lip 28 covered by the aluminum 26a is less per gram of aluminum evaporated than is the amount of heat, per gram of aluminum evaporated, radiated by the aluminum 26 in the crucible. This is due to the fact that, for any given temperature in the crucible, the aluminum 26a on the lip is somewhat hotter than the aluminum in the crucible, and therefore the total heat transferred to the substrate by the vapors emanating from aluminum 26a will be indicated by a point on the curve B corresponding to the temperature of aluminum 26a.

With a device of the type schematically shown in Fig. 2, it is possible to obtain evaporation rates above 4 grams per minute per square inch of surface area at the top of the molten aluminum within the body portion 24. This high evaporation rate is readily achieved when operating at chamber pressures of about 0.2 micron and at aluminum pool temperatures on the order of 1350° C.

Referring now to Fig. 3 there is shown a modification of the present invention which is particularly adapted for coating extremely heat-sensitive materials, such as thin tissue papers, plastic coatings having high plasticizer content, and the like. In the Fig. 3 embodiment of the invention several coating stages are provided, two being shown in the modification illustrated. With this arrangement, the total heat reaching the substrate at any particular stage in the coating is maintained low enough so that the sub-

strate is never heated to a temperature sufficiently high to cause outgassing. Since, as explained previously, the total heat is a function both of the radiant heat and the heat carried over by the vapors, it is apparent that, when operating at the relatively high vapor temperatures preferred, the total heat may be decreased only by decreasing the quantity of vapors actually reaching the substrate.

In the Fig. 3 embodiment of the invention, the substrate is first coated with a thin aluminum coat at high vapor temperatures. The substrate is then cooled to remove the heat carried to the substrate. The final coat is then applied by passing the substrate over a second source of vapors. If the first coat is sufficiently thick to give a very high reflectance, on the order of 70%, the radiant heat being transmitted to the substrate during the second coating is relatively less important since the majority of this radiant heat will be reflected by the coat previously applied to the substrate. Consequently, the temperature of the vapors of the second source may be somewhat lower than the temperature of the vapors of the first source. However, it should be apparent that the total heat reaching the substrate, even in the second coating operation, will be less with higher vapor temperatures.

Referring now to Fig. 3 in detail, it can be seen that like numbers correspond to like elements of Fig. 2. In this figure the chamber 10 is indicated as defining chambers 12, 12a, 12b, and 12c, chamber 12 being a coating chamber similar to that of Fig. 2 and containing the two concentric crucibles 22 and 40 and the heating coil 32. Chamber 12a is a second coating chamber including a similar arrangement of elements such as the crucible 22a. Chamber 12b is a cooling chamber, and chamber 12c is a windup chamber. These various chambers are defined by partitions 44 which prevent undue migration of vapors from one coating stage to another to prevent coating of the various cooling and measuring devices hereinafter described. Holes 46 in the partitions 44 permit evacuation of all chambers by the single pumping system 14. Within the cooling chamber 12b there is provided a plurality of cooling coils 48 and a pair of cooling and feeding rolls 50. Within the windup chamber 12c there is provided a pair of rolls 52 connected to a resistance measuring circuit 54. The resistance measuring circuit 54 is connected to a meter, speed control device, or a crucible temperature control device. The design and operation of such a system is more fully described and claimed in the copending application of Godley, Serial No. 10,117, filed February 21, 1948, now U. S. Patent No. 2,545,576.

In the operation of the device of Fig. 3 the roll of substrate to be coated is positioned on spool 16, fed through the various openings in the partitions 44, and wound on the takeup spool 18. The chambers are evacuated and the two crucibles 22 and 22a are heated to vaporize the aluminum. In a preferred form of the invention, the aluminum in the crucible 22 is heated to a high temperature such that its vapors have a temperature above 1300° C. so that the amount of radiant heat approaching the uncoated substrate is relatively minor with respect to the total heat reaching the substrate from the vapors condensing thereon. If the coating applied in the first coating chamber 12 is sufficiently thick so as to give a reflectance of about 70% or more, the temperature of the vapors emanating from

the second crucible 22a can be relatively low, on the order of 1200° C. or thereabouts. However, it is preferred that the temperature of these vapors be 1250° C. or above. When the coating applied in the first chamber is relatively thin so that the reflectance of the film is relatively low, such as about 50%, it is preferred that the temperature of the vapors emanating from the second crucible 22a be on the order of 1300° C. and above.

In the various embodiments of the invention illustrated, the heating means comprises the induction coils 32. This heating may be achieved in many other ways well known in the art, such as resistance heating within the aluminum, radiant heating of the aluminum or the crucible, and combinations of these and other systems of heating.

The coating control means of Fig. 3, comprising the resistance measuring rolls 52 and the control circuit 54, may equally be used in the Fig. 2 embodiment of the invention. Additionally, the coating in the Figs. 2 and 3 devices may be controlled by reflectance measuring means, such as that shown in U. S. Patent No. 2,490,084. In this form of the invention, the measured reflectance can be used to control the heat of the aluminum, the speed of the substrate, or merely give a visual indication to the operator.

In the type of crucible shown in the drawings, the effective evaporating area is considerably larger than the area of the top of the molten pool in the crucible. It should be pointed out that, in those cases where the mouth of the crucible is smaller than the pool of metal carried thereby, the effective evaporating surface is smaller than the surface of the molten pool (assuming no climbing of the aluminum out of the mouth) and the temperature of the vapors issuing from the mouth controls the rate of aluminum vapor emission from the crucible.

Since certain changes may be made in the above process 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 drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for coating a heat-sensitive substrate by vacuum-evaporating aluminum and condensing aluminum vapors on the substrate, said process comprising the steps of providing a source of aluminum in a vacuum chamber, evacuating said chamber, melting said aluminum to form a pool of molten aluminum, heating said aluminum to a temperature such that the aluminum vapors leaving said source have a temperature between about 1300° C. and about 1500° C., moving said substrate past said source at a speed adjusted to give a substantially uniformly thick coating having a reflectance for visible light on the order of 90%, and limiting the radiant heating area, which is in the neighborhood of said source and which does not evaporate aluminum, to less than the effective evaporating surface area of the molten aluminum from which the aluminum vapors are derived by spreading said molten aluminum outwardly from the molten aluminum pool to cover hot areas of the source which would otherwise radiate heat to the substrate without contributing aluminum vapors.

2. A process for coating a heat-sensitive substrate by vacuum-evaporating aluminum and condensing aluminum vapors on the substrate,

said process comprising the steps of providing at least one source of aluminum vapors in a vacuum chamber, evacuating said chamber, melting aluminum in said source to form a pool of molten aluminum, heating the effective evaporating surface of said aluminum vapor source to a temperature between about 1300° C. to 1500° C., moving said substrate past said source at a speed adjusted to give a substantially uniformly thick coating, and limiting the transfer of radiant heat to said substrate by covering with a layer of molten aluminum more than half of the hot area of the source which is in position to radiate heat to the substrate, and maintaining said molten aluminum layer at said high temperature of between about 1300° C. and about 1500° C.

3. A process for coating a heat-sensitive substrate by vacuum-evaporating aluminum and condensing aluminum vapors on the substrate, said process comprising the steps of providing a source of aluminum in a vacuum chamber, evacuating said chamber, melting said aluminum to provide a molten body of aluminum, heating said molten aluminum to a temperature between about 1300° C. and about 1500° C. to vaporize said aluminum, moving said substrate through said vapors at a speed such as to give a relatively constant thickness of coating of condensed aluminum thereon, and spreading said molten aluminum outwardly from said molten body to cover, with molten aluminum, heat-radiating surfaces which would otherwise radiate heat to the substrate without contributing aluminum vapors to limit, to a total effective radiating area less than the effective evaporating area of the surface of the molten aluminum, all those areas of non-evaporating, heat-radiating surfaces which are in the neighborhood of the source, which are at a temperature near the temperature of the molten aluminum, and which are in a position to radiate heat to the substrate.

4. A process for coating a heat-sensitive substrate by vacuum-evaporating aluminum and condensing aluminum vapors on the substrate, said process comprising the steps of providing at least one source of aluminum in a vacuum chamber, evacuating said chamber, melting said aluminum in said source to provide a molten aluminum body, heating said molten aluminum in said source to a temperature such that the aluminum therein is evaporated, maintaining at a temperature between about 1300° C. and 1500° C. those vapors leaving said source which coat said substrate when it has a reflectance less than about 70%, limiting the amount of radiant heat reaching said substrate, prior to the time when said substrate has a reflectance of about 70%, to not much more than the amount of heat carried to said substrate by said vapors by spreading said molten aluminum outwardly from said molten aluminum body to cover at least half of the hot areas of the source which would otherwise radiate heat to the substrate without contributing aluminum vapors, and moving said substrate past said source at a speed adjusted to give a substantially uniformly thick coating having a reflectance for visible light of at least 70%.

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