

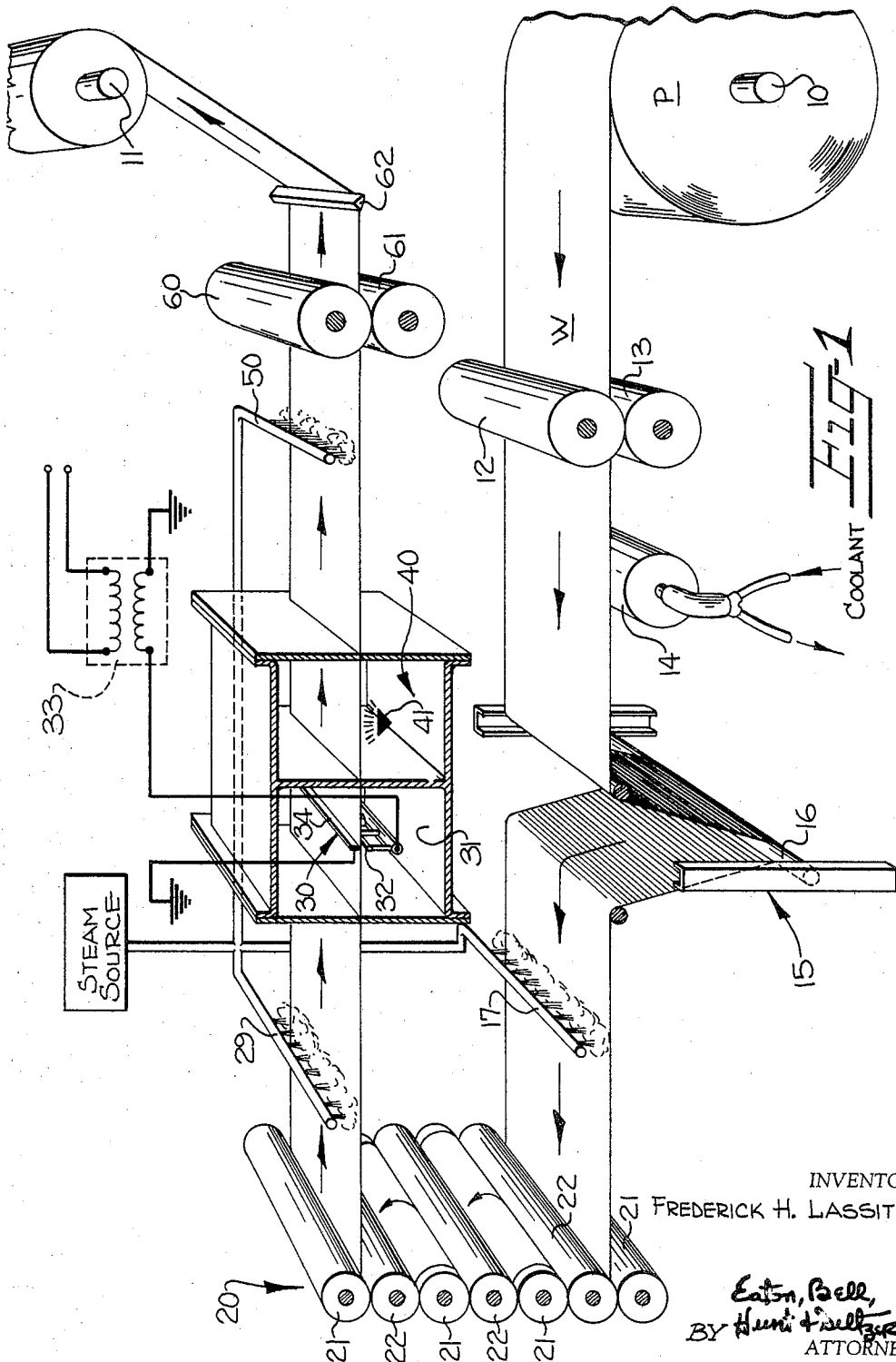
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METAL COATED PAPER EMPLOYING IRRADIATED SUBBING LAYER

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**METAL COATED PAPER EMPLOYING
IRRADIATED SUBBING LAYER**

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This invention relates to metal coated products, and more particularly, to fibrous products having an adherent, metallic film and a method of producing such products. This application is a continuation-in-part of my copending application Serial No. 809,549, filed April 28, 1959, now abandoned and entitled Method of Producing Reflective Metal Appearances on Substrates and Resulting Products. The instant invention is an improvement thereon and is primarily directed to facilitating the obtaining of high reflectivity and brilliance of the vacuum deposited metal film on fibrous products, such as paper, by reducing the dependency of calendering the same after metallizing for obtaining the desired high reflectivity and brilliance.

As pointed out in my aforementioned application, there has been much effort exerted in the paper industry toward finding an economical replacement for metal foil laminated paper products. These activities have primarily centered around using a vacuum deposited film of metal in lieu of a relatively expensive sheet of foil, thus reducing the cost of raw materials as well as eliminating the step of laminating. This film of metal is generally deposited with a thickness of approximately 3 to 5 micro-inches, while foil sheets are generally limited to a *minimum* thickness of approximately 350 microinches.

Heretofore, the attempts by others to vacuum metallize paper products have always been plagued with the problem that the metal film is so thin that it faithfully follows the surface characteristics of the paper substrate. And, since paper is of a fibrous nature and therefore, as a rule, lacks a highly specular surface, the metal film did not exhibit the often desired degree of reflectivity and brilliance. The initial approach to solving this problem was to provide the paper substrate with a coating of a plastic or resinous nature which would (1) be receptive to the metal film and provide adequate adhesion between the coating and the metal film, (2) be compatible with the vacuum metallizing operation, and (3) provide a highly specular surface for the reception of the metal film to permit obtaining the desired brilliance and reflectivity thereof.

It is apparent, however, that the necessity for the addition of such coatings added many undesirable characteristics to such metallized paper products. For example, the added coating increases the cost of raw materials and of manufacture of the product and thus brings the cost of such product up to the undesirable high cost level of the laminated foil product. Additionally, such coatings form an impervious barrier on the underlying surface of the substrate, thus permitting moisture to enter the product *only* from the uncoated surface, and thus creating a substantial curling problem. Also, this impervious barrier fails to eliminate many of the problems in printing which are present with laminated foil products as well as with numerous vacuum metallized products, and thus necessitates great care in the selection of inks and restricts the types of printing methods available for such products as well as restricts the printing speed and number of colors which can be printed at one time.

In my aforementioned application, I point out that the necessity for forming a highly specular paper surface through the use of such coatings can be eliminated by relying upon calendering *after* metallizing for attaining the desired brilliance and reflectivity of the metal surface, with the result that the problem of imperviousness is

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eliminated and the cost of the end product substantially reduced.

In addition to the plastic or resinous coated papers referred to above, there are other known paper products which also possess a high degree of specularity. Such papers can be classified generally as glazed papers and have been widely used in the decorative paper field because of their high specularity. These glazed papers are manufactured generally by one of two glazing or polishing processes. One such process is known as "friction glazing" or "friction calendering" and involves passing the paper through the nip of one or more pairs of rolls wherein one of said rolls is oversped to, in effect, polish the contacting surface. The other such process is known as "flint glazing" and involves passing a surface of the web into contact with a shaped flint stone which is reciprocally moved laterally across the supported web at high speeds, to also, in effect, polish or iron the contacting surface. After each of such processes, if desired, such papers can be further treated in various manners known to those skilled in the art to impart different properties thereto. For example, such papers can be supercalendered to further increase surface specularity.

In each of the above-outlined processes, it has always been necessary to introduce a slip agent of wax components into the paper prior to such frictioning operation in order to avoid rupturing the paper. Thus, while these glazed papers present high surface specularity, they are nevertheless unacceptable for vacuum metallizing due to the fact that the wax used in the friction polishing operations prevents adequate adherence of a subsequently deposited metal film.

I have discovered, however, that such highly specular glazed papers can be so treated and modified that subsequently deposited metal films will attain a high degree of adherence thereto, without diminishing the high reflectivity and brilliance, which fully meet trade requirements.

This modification is effectuated by a change in the characteristics of the glazed papers, and is accomplished by subjecting the waxy glazed surface of the substrate to a high energy electron irradiation treatment, such as a corona or glow discharge. Surprisingly, I have found that such treatment does not noticeably lessen the specularity of the substrate (as evidenced by no visible lowering of the reflectivity and brilliance of the subsequently deposited metal film), while at the same time, it does change the characteristics of the glazed surface to the extent that the adherence of the metal film thereto is vastly improved.

With the foregoing background material in mind, it is a primary object of this invention to provide a new and novel metallized product and a method of forming the same.

Another object of the invention is to utilize paper substrates with waxy surfaces thereon for forming metallized products having acceptably adherent metal films thereon.

Still another object of the invention is to utilize highly specular conventional paper substrates with waxy surfaces thereon for forming metallized products of high reflectivity and brilliance while attaining commercially acceptable adherence of the metal thereto.

A more specific object of the invention is to subject a highly specular fibrous substrate having a waxy surface thereon to the physical treatment of high energy electron irradiation to cause such surface to be so altered, to provide vastly improved adherence characteristics for a subsequently deposited metal film.

An additional object of the invention is to enhance the reflectivity and brilliance of the deposited metal film by calendering the metal film and to provide such other treatments thereto as may be desired, such as embossing.

Some of the objects of the invention having been stated, other objects will appear as the description proceeds, when taken in connection with the accompanying drawing, in which:

The figure schematically represents a mechanism for continuously treating a fibrous substrate to attain the desired product of this invention.

Referring now specifically to the drawing, reference numeral 10 designates a let-off roll which carries a roll of paper P with W representing a web portion extending therefrom and traveling in the direction indicated by the arrows under the ultimate impetus of a take-up roll 11, and upon which roll the web is suitably rewound after being processed in accordance with my invention. As shown, the web W is initially directed between the nip defined by a pair of calender rolls preferably comprising an upper steel roll 12 and a lower resilient roll 13. These rolls cooperating together serve to impart a friction calendering action on the upper surface of the web. This is accomplished by driving the upper steel roll 12 at a higher peripheral speed than the linear speed of the web, preferably about two and one-half times as great, with the result this roll exerts a polishing or rubbing action on the upper surface of the web. The speed of the lower roll 13 is approximately the same as the linear speed of the web. With respect to this step of glazing with friction calender rolls, it is to be understood that such step could also be accomplished with conventional flint glazing equipment as generally described previously herein.

To avoid rupture of the web by virtue of the friction created by the action of roll 12 thereagainst (or the shaped flint stone thereagainst in instances where flint glazing equipment is employed) a lubricant or slip agent, such as wax, is added to the paper prior to this friction calendering operation. This is normally accomplished by intermixing the slip agent with the components of a conventional paper clay coating. When the slip agent employed is wax, the wax usually consists of about 3% to 8% by weight of the clay coating and the following examples illustrate wax containing paper coatings which have been successfully employed in practicing the instant invention. These examples are given by way of illustration only, and are not intended in any way to limit the scope of the invention. Parts are by weight.

Example I

5 parts carnauba wax is melted with just enough heat to melt the wax. 2 parts of oleic acid and 0.375 part of a surface-active agent such as Duponal WS (a Du Pont trademark for a surface-active agent of the alcohol sulfate type) are then mixed in with the wax. 0.35 part of caustic soda dissolved in 1.25 parts water are then added. Finally, 41.0 parts of boiling water are added and the ingredients are agitated for 15 minutes to form wax emulsion A.

A coating composition is then prepared according to the following formula and then coated on a base paper:

	Parts (dry)	Parts (wet)
Lustra Clay.....	279.5	419.0
Mistron Talc.....	24.3	50.1
Casein (ammonia cut).....	48.9	285.5
Wax Emulsion A.....	21.65	148.2
Rhoplex B-15.....	9.14	20.4
Water.....		184.12
Tri-butyl-phosphate.....	1.37	622.0
P947.....	1.23	1.37

Lustra clay is marketed by the Southern Clay Company. Mistron talc is an ultra-fine particle size magnesium silicate manufactured by Sierra Talc & Clay Co. Rhoplex B-15 (a trademark of Rohm & Haas) is an aqueous dispersion of an acrylic resin. P947 is a defoaming agent manufactured by the Pioneer Chemical Company.

Example II

50 parts of a petroleum base oxidized wax such as Duroxon J324V are added to 198.65 parts of water having a temperature of 185° F. 1.35 parts ammonia dissolved in 18 parts water are then added followed by the addition, with stirring, of 4.5 parts oleic acid. The temperature is then raised to 215° F. and, after about 20 minutes the ingredients are agitated for about 30 minutes, to form wax emulsion B.

A coating composition is then prepared according to the following formula and then applied to a base paper.

	Parts (dry)	Parts (wet)
Lustra Clay.....	333.5	488.0
Mistron Talc.....	29.0	59.8
Casein (ammonia cut).....	57.5	415.0
Wax Emulsion B.....	18.2	89.5
Rhoplex B-15.....	10.9	24.35
Water.....		212.78
Tri-butyl-phosphate.....	1.76	800
P947.....	1.59	1.76

Returning again to the drawing, it is desirable that a temperature of about 200–350° F. be maintained during the friction calendering operation. Thus, the rolls 12 and 13 are hollow and may be cooled or heated by any conventional manner as desired, depending upon the heat being generated by their working action on the web.

Since the rolls 12 and 13 are normally arranged to impart 500 to 1500 pounds pressure per linear inch on the web, this working action of the rolls, plus the heat being supplied to or generated by the rolls, serves to work the wax slip agents to provide a highly specular surface on the web.

The thus friction glazed paper web is now directed into contact with a cooling roll 14 which serves to dissipate the heat created in the web by the friction polishing operation. Subsequently, the web is passed through a conventional dancer roll arrangement, broadly indicated at 15, which serves the function of a slack tensioner device under the action of a vertically movable roll 16, the position of which is determined by the tension in the web.

The web, after leaving the dancer roll arrangement, is desirably directed past a steam or moisture station 17 for the purpose of restoring to the web moisture which has been dissipated by the friction calendering operation.

The addition of moisture to the web at this time serves to avoid brittleness of the web and protects the same during a subsequent supercalendering operation performed by a plurality of stacked rolls broadly indicated at 20. To aid in obtaining the desired working action on the paper surface to smooth and compact the same, these stacked rolls may be internally heated to a temperature of about 350° F. to 450° F. As illustrated, the web is directed through the nip formed from the two bottom-most rolls of the stack and then is suitably threaded in a sinuous path through the nips of the rolls, with the web being directed away from the supercalendering operation between the uppermost nip of the rolls.

The stacked rolls 20 are driven at the same speed as the web and are preferably arranged with alternate rolls 21 being formed of a hard, resilient material, such as plastic or rubber, and intervening rolls 22 being formed of steel, with the result that each nip through which the web is laced is defined by a cooperating pair of resilient and steel rolls. Furthermore, it should be noted that the steel rolls 22 engage the previously friction glazed surface of the web, while the resilient rolls 21 engage the back side thereof with the result that the smoothness and specularity of the thus treated web surface is substantially improved.

At this point the web so processed in accordance with the foregoing, without further treatment may be classified generally as a conventional friction glazed paper which has been supercalendered. As pointed out above, if this

paper were now subjected to a vacuum metallizing treatment, in many instances such metallized product would have a highly brilliant reflective metal surface. However, such product, without further treatment, is for the most part unacceptable for commercial usage since the metal film lacks proper adherence to the glazed substrate because of the wax. This lack of metal adherence, I have found, is readily evident by simply sticking a piece of pressure sensitive tape on the metal surface and thereafter removing the same (commonly known in the paper industry as a "Scotch Tape" test). Upon removal of the tape, a substantial amount of metal is pulled off the substrate therewith.

Returning again to the drawing, the web emanating from the nip of the upper pair of supercalendering rolls may be directed past a second steam or water station again to restore moisture to the web driven therefrom by the supercalendering operation. It should be noted that the manner in which the web is directed away from the uppermost pair of calender rolls, positions the specular surface of the web facing downwardly.

The web is now directed to a high energy electron irradiation source, such as a corona or glow discharge apparatus, broadly indicated by reference numeral 30 which acts on the full width of the web. The irradiation source, as shown in the drawing, is carried out in a partial vacuum compartment 31 which can have a pressure in the neighborhood of 3 to 1,000 microns of mercury. It should be understood, however, that such irradiation treatment can also be accomplished under atmospheric conditions.

The corona discharge apparatus schematically shown comprises an elongate electrode 32 positioned beneath the path of travel of the web and close to the web to thus act on the glazed surface thereof. Preferably, the spacing between the electrode and the web should be between $\frac{1}{4}$ and 10 inches. The electrode 32 is suitably energized from a source of electric potential, here illustrated as a transformer 33. An elongate grounded bar 34 of similar length is provided to engage the upper surface of the web which bar may be provided with a dielectric covering, if desired.

As is well known, corona discharge occurs when air or gas is subjected to a potential gradient sufficiently high to ionize it. When air is ionized, it becomes a conductor capable of carrying current. Thus, when the electrode 32 is energized with suitable voltage, a corona occurs across the width of the web. Based upon actual experiments, I have found that highly satisfactory adherence of subsequently deposited metal films is achieved when the treatment of the glazed web is performed under vacuum conditions of 30 microns of mercury wherein the web is subjected to about one (1) ampere of current per linear inch of web width when traveling by the electrode at a speed of from 140 to 600 feet per minute. Such current has been produced by impressing about 300 to 450 volts upon the electrode at a frequency of 60 cycles per second. Experiments have also been performed under partial vacuum conditions by increasing the voltage up to 7,000 with satisfactory results being obtained with the use of only .015 ampere of current at similar speeds.

Additionally, glazed papers have been subjected to high energy electron irradiation at atmospheric pressure with a Lepel High Frequency Spark Generator, Model HFSG-2, at a speed of 100 feet per minute. After metallizing, such treated papers exhibited substantially improved metal adherence characteristics. This generator was manufactured by Lepel High Frequency Laboratories, Inc., and has a spark gap energized primary circuit with a tuned secondary output circuit; a power input of a maximum of 1.5 kw. at 115 or 230 volts, single phase, 60 (or 50) cycles; and a frequency of approximately 450 kc.

From the foregoing examples of high energy electron irradiation it is readily seen that such irradiation can be

produced in various ways, and that the conditions under which such treatment is to be applied can be determined by routine experimentation by those skilled in the art.

Returning again to the drawing, after the specular surface of the web has been irradiated, the web is directed into an adjoining vacuum metallizing chamber, broadly indicated at 40, which contains a suitable source of metal 41 for forming a desired metal film on the web. This metal film is generally deposited at a thickness of approximately 3 to 5 microinches under vacuum pressures of $\frac{1}{2}$ to 3 microns of mercury as when the metal employed is aluminum. Other metals such as zinc, for example, can also be used.

While it is preferred to carry out the irradiation treatment of the glazed paper and the metallizing thereof in a continuous operation, as schematically illustrated in the drawing, for reasons of apparent economy, it is evident that the invention is not restricted to such a continuous operation. However, it might be mentioned that such a continuous operation would serve to reduce the time between the irradiation treatment and vacuum metallizing operation. While under most expected commercial conditions this would not be of vital importance, it may nevertheless be advantageous under certain conditions of irradiation treatment and/or with certain formulations of the coating used in forming the glazed surface of the paper.

The web, after being metallized is directed outside of the vacuum chamber 40 and preferably past a third steam or water station 50, again to replenish moisture removed from the web by the vacuum metallizing operation. The thus treated web is now directed between the nip defined by upper and lower calender rolls 60, 61 respectively, with the lower roll 61 preferably being a mirror finish roll to impart added reflectivity and brilliance to the metal film, when the necessity arises. These rolls 60, 61 are driven at substantially the same peripheral speed as the linear speed of the web. Such after-calendering operation of the metal film is explained in considerably more detail in my aforementioned copending application. The web is then passed underneath a curl correcting bar 62 to remove any tendency of the web to curl and is then suitably rewound in roll form by the take-up roll 11.

A variety of tests on a wide variety of papers have clearly shown that, in the absence of the irradiation treatment to the glazed surface, the deposited metal film is readily separated from the paper substrate. However, on the contrary, when such papers are subjected to an irradiation treatment prior to metallizing, they exhibit greatly enhanced adherence qualities, thus rendering the product commercially marketable. Some of such tests used to show this difference of adherence are, for example, the "Scotch Tape" test, the "Dennison Wax" test and the "Split Ink" test, all of which are well known in the paper industry.

Although the description of the invention herein has been primarily concerned with the adherence of metal films, it should be noted that it has been found that irradiation treatment of the waxy surface of glazed papers also greatly enhances the adherence of subsequently deposited inks, such as those used in offset printing, for example.

It is thus evident that I have provided a novel process and product wherein conventional papers having waxy surfaces can be used, which papers heretofore could not be utilized to form a suitable metallized product. This is accomplished by irradiating the waxy surface of such papers to modify the same and thereby to adherently receive a metal film thereon. Further, it is apparent that one very important ramification of this invention is the opening of many new markets for these types of conventional papers which heretofore have been virtually useless in this field due to their inability to adherently receive a metal film thereon.

In the drawing and specification, there has been set forth a preferred embodiment of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being defined in the claims.

I claim:

1. A method of forming an adherent metal film on a glazed coated paper substrate coated with a formulation containing clay, magnesium silicate, casein, an aqueous dispersion of an acrylic resin, tri-butyl-phosphate, a defoaming agent, and an emulsified wax selected from the group consisting of petroleum base oxidized wax and carnauba wax, said method comprising the steps of modifying the glazed surface of said substrate to improve substantially the metal adherence characteristic thereof by subjecting said surface to high energy electron irradiation and depositing under high vacuum conditions a micronically thin metal film on the modified surface.

2. A method according to claim 1 including the step of calendering the metal film.

3. A method according to claim 1 wherein the vacuum deposited metal film is aluminum.

4. A method according to claim 1 wherein the high energy electron irradiation is performed in the atmosphere.

5. A method according to claim 1 which includes the step of supercalendering the glazed coated paper prior to irradiating the same to further improve the specularity thereof.

6. A method according to claim 1 wherein the high energy electron irradiation emanates from a corona discharge.

7. A method according to claim 1 wherein the high energy electron irradiation emanates from a spark generator.

8. A method according to claim 1 wherein the high energy electron irradiation is performed under partial vacuum conditions.

9. A method according to claim 8 wherein said high energy electron irradiation emanates from an electrode impressed with about 300 to 450 volts and producing a current of about one ampere per inch of substrate width.

10. A metallized product comprising a glazed paper substrate having a coating on a surface thereof containing clay, magnesium silicate, casein, an aqueous dispersion of an acrylic resin, tri-butyl-phosphate, a defoaming agent, and an emulsified wax selected from the group consisting of petroleum base oxidized wax and carnauba wax, said coated surface being modified by irradiation to improve its metal adherence characteristics and a strongly adherent micronically thin metal film on said surface in intimate, contiguous engagement therewith, the adherence of said film being characterized by a greater overall affinity for said surface than by pressure sensitive tape applied thereto in accordance with the "Scotch Tape" test defined herein.

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