

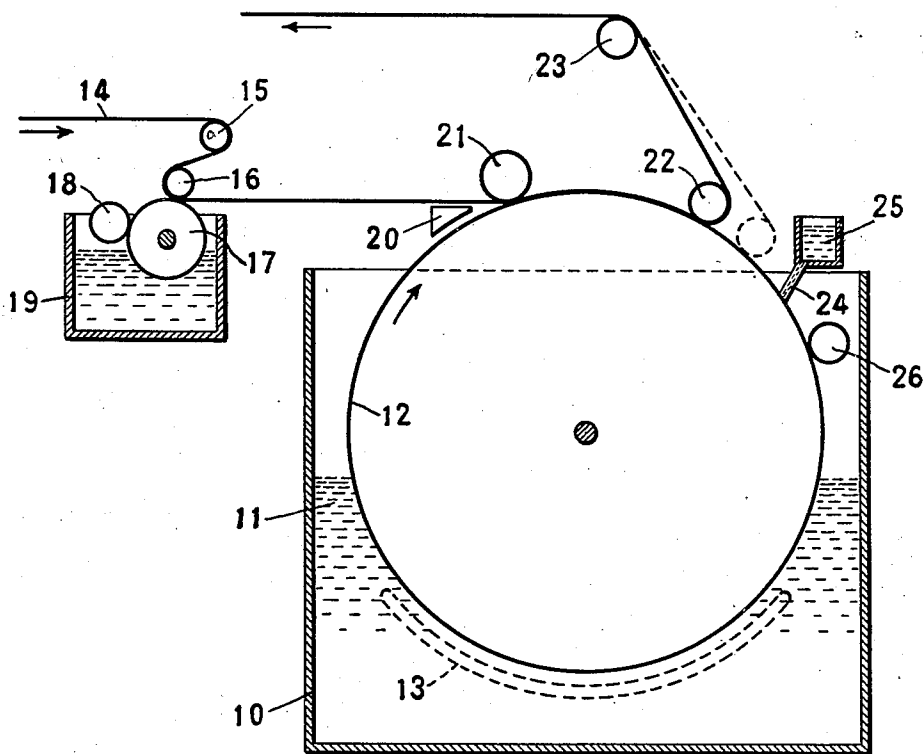
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MANUFACTURE OF METAL COATED PAPER

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MANUFACTURE OF METAL COATED PAPER

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This invention relates to metal coated paper and has for its object to render the production cost of such material low enough for the article and its process of manufacture to become commercial.

Another object is to reduce the thickness of an electrodeposit metal layer which may be continuously removed from a moving cathode.

Heretofore an electrodeposit metal layer of copper, for example, has been stripped from a moving cathode when such metal layer has a thickness of about .0013 inch. Much thinner electrodeposit layers have been desired but have not been commercially available for a number of reasons.

One difficulty has been in the stripping of the thin layers of metal from the cathode owing to the danger of the thin metal getting ruptured in its removal from the cathode. Lead and lead alloys are common materials for the cathode surface on which layers of copper and other materials have been electrodeposited. Efforts have been made to find other cathode surfaces from which thin layers of metal can be stripped with less tension and with greater ease than they can from a lead surface but such other surfaces possess disadvantages. For example, a stainless steel cathode surface has been found to facilitate removal of a thin layer with greater ease but this material does not lend itself for surfacing of commercial cathodes.

If a cathode is flexible stainless steel it is difficult and expensive to make in this form. If the cathode is a rigid rotating drum it is difficult to have a stainless steel surface which may be uniformly and highly polished without any imperfection or unevenness such as results from a welded joint. The high polish on the cathode surface determines to a large extent the appearance and finish of the electrodeposit layer which is formed thereon. The rotatable drum type cathode must generally be large in diameter in order to provide the length of surface required for electrodeposition at a satisfactory rate and still have the drum move fast enough for the process to be commercial.

With a large diameter drum a stainless steel surface which is drawn or seamless is expensive and difficult to provide. The difference in composition of a stainless steel surface at a welded joint makes uniform high polishing difficult because the composition of the material is generally different at the welded joint from what it is elsewhere and such difference in composition causes a difference in polish or finish at the welded joint.

In times past the use of various chemical films was suggested between the deposit layer and the cathode in order to make stripping easier but these have not been found satisfactory.

A knife has also been suggested to facilitate stripping but this has not been found satisfactory because it is either in danger of scratching the cathode surface with the result that heavy polishing is made necessary before the cathode surface can be again used, or else the knife is in danger of taking off some of the lead or other cathode surface with the electrodeposit layer.

The use of paper and an adhesive attached to the deposit layer on the cathode has been suggested with the use of some of the aforementioned chemical films between the cathode and deposit layer. So far as is known no one has heretofore used paper which is stronger than the metal layer so that the paper may transmit the major portion of the tension necessary to strip the metal from the cathode and thus lessen the hazard of a thin metal layer breaking. Possibly one reason why paper has not been so used before may be the selection of an adhesive. Ordinary fish or animal glue takes so long to dry that commercial production is slowed up and rendered difficult. If such adhesive is made to dry too quickly it becomes crystalline and brittle so that the adhesive may crack or break with danger of a crack or break in a metal layer held to paper by the adhesive. Ordinary gummed paper was only moistened and tried as a foundation for an electrodeposit layer but this was not found satisfactory because the gum was likely to release the metal layer when it got moist again.

Adhesives in solution were tried which are of the type that do not become again soft when wet but these were open to the objections possessed by the fish or animal glues mentioned above as lacking satisfactory flexibility.

It has been found that many of the resinous adhesives may be rendered sufficiently flexible by the addition of a plasticizer and it has also been found that when adhesives of this type are applied hot and allowed to set on cooling advantageous results accrue. For one thing such adhesives may not permeate the fibrous foundation as much as do those applied with solvents and they may be set more quickly. An especially desirable result is believed due to the different effect which cooling has upon the fibrous foundation and the metal layer, the foundation tending to expand by the absorption of moisture whereas the metal layer shrinks on cooling.

While such effect imposes an added reason for

a flexible adhesive it contributes to satisfactorily holding the metal layer stretched tightly on the paper. Although these advantages are generally inherent in a flexible adhesive which is applied hot and which sets on cooling, they may be present with the use of solvent types of adhesives if heat is applied to expedite setting and the foundation dried thoroughly so that it will tend to expand and absorb moisture on cooling, and also if the heating is sufficient to cause substantial contraction of the metal layer without this shrinkage being too great and in danger of rupturing the metal layer.

It has further been discovered that a sharp melting point adhesive applied hot is especially adapted for use with rotating cathodes where only a short time is available for the adhesive to set before it must be stripped from the cathode when such is moving at a commercial speed.

According to this invention a thin layer of metal such as copper is deposited on a moving cathode. After the cathode has been freed of any electrolyte on its surface an adhesive coated paper is pressed against the metal layer on the cathode. The cathode and paper are moved together until the adhesive has set enough to permit the paper and metal layer being pulled off together or stripped from the cathode. For this purpose the paper must be stronger than the metal layer so that where very thin or fragile layers are used the paper may transmit most of the tension necessary to strip the metal from the cathode. The side edges of the metal layer should be cleaned or freed of any metal which has deposited or which tends to deposit on the side edges of the cathode.

Before being stripped the paper and metal coat are substantially heated so that as the adhesive sets the metal coat is stretched tight over the paper by shrinkage. This heating should be to a temperature below that at which the paper chars and also below that at which the contraction of the metal layer may be so great as to cause its rupture. This element of heating is therefore more vital with thin metal layers than with those which are much thicker. Since the paper after being dried tends to absorb moisture and expand, it will be understood that a flexible adhesive is therefore necessary to stand the stretching imposed upon it by the expansion of the paper at the same time the metal layer may be contracted on cooling.

The single figure of the drawing is a diagrammatic view of apparatus for carrying out the process and producing the article of this invention.

In the drawing there is provided a tank 10 for electrolyte or the bath. The cathode in the embodiment illustrated is a rigid rotating drum 12 on the periphery of which a layer of metal is electrodeposited either from the bath or from an anode 13. In order to make the periphery long enough for the metal to be deposited in a satisfactory manner the drum is about twelve feet in diameter and about thirty one inches wide, having a speed of about nine feet a minute or roughly about fifteen revolutions per hour.

Appropriate means are provided to prevent the deposition of any metal upon the side edges of the drum, or in other words the side edges of the cathode are kept clean to prevent deposition of any metal on them so that the later removal of the electrodeposit metal layer from the drum is not impeded by any bond between the metal layer and a deposit on the sides of the drum.

Instead of keeping the sides of the layer and cathode clean during the depositing operation, the sides of the cathode may be later cleaned by cutting off any deposit which has formed, but this latter method is not preferable with a rotating drum type cathode.

After leaving the electrolyte the deposit layer on the cathode is wiped and washed by appropriate apparatus, not illustrated. A roll of paper, not shown, is being continuously unwound, the paper 14 traveling over the tension roll 15 and thence around a roll 16 which presses the paper against an applicator roll 17 for coating the same with an adhesive. The applicator roll is provided with the usual doctor roll 18 and a supply tank 19 containing the adhesive in liquid form.

In order to obtain the quick setting adhesive necessary for use with a rotating drum type cathode the adhesive is of the type which is adapted to set on cooling, it having a sharp melting point. Due to the quick setting of the adhesive which takes place between its application to the paper and the cathode 12, it is necessary to provide a reheating device 20 for the adhesive coat on the paper, and this reheater may be either in the form of a smoothing roll or a heated surface over which paper is passed immediately before it is brought in contact with the electrodeposit layer on the cathode.

The paper is pressed against the metal layer on the cathode by the pressure roll 21. The pressure of roll 21 against the cathode is made adjustable in some convenient manner. After contacting with the rotating drum the paper with the adhesive between the paper and the layer of metal moves with the cathode until the adhesive has had a chance to set sufficiently so that it adheres to the layer of metal strongly enough for the metal layer to be pulled off or stripped from the drum by the paper, most of the tension necessary for the stripping operation being transmitted to the metal layer through the paper. After passing around the drum for a short distance the paper then passes around the stripping roll 22, by which time the adhesive has set sufficiently for the layer of metal to adhere to the paper and to be pulled off the drum by the paper. After passing around the stripping roll 22 the paper is then directed around a guide roll 23 and onto a winding roll, not shown.

The coating operation may take place at a much faster speed than is desirable for the cathode so that the coating operation may be done at a remote point and the coated paper then supplied directly to the cathode with a heater of some sort used to melt the adhesive ready for it to set in contact with the metal layer. The adhesive in the tank 19 is heated to about 250° F. and the reheater is adapted to heat the adhesive again to at least this temperature as well as function to even out or smooth the adhesive.

The pressure roll 21 has a rubber or other equivalent periphery which is likewise heated at about 225° F. to 250° F. The stripping roll 22 is preferably yieldably mounted so that it may move with the cathode in case the paper should stick, the dotted line position indicating how this roll 22 is capable of moving with the cathode when necessary. Preferably the stripping roll is under spring or other tension and hooked up with the rewinding mechanism so that it may yield or give a little, the stripping roll 22 being 75

geared to the winder so that the paper is always under tension.

The paper used is about thirty-two inches wide, or, in other words, wider than the metal layer on the cathode in order that it may overhang the edges of the cathode and give additional strength for pulling the edges of the metal layer off the cathode, inasmuch as the edges are often inclined to stick and require a stronger pull for stripping them than is necessary for the intermediate portions of the metal layer between its side edges.

After being stripped the cathode is then wiped by a wick 24 saturated with a liquid solvent from the tank 25 for the purpose of cleaning the drum surface of any particles of adhesive from the paper previous to its being stripped. After having its surface cleaned in this manner it may be dried by a wiper or in any other manner and then before re-entering the bath the cathode surface is again highly polished by the oscillating burnisher 26.

With a rigid type cathode the drum surface is preferably of lead or lead alloy and the polishing is of such a nature that it tends to gradually wear down the surface of the drum.

The degree of polish imparted to the cathode surface prior to the deposition of the metal layer is extremely important since the character of the cathode surface determines not only the ease with which the deposit may be stripped, but it also determines the smoothness and appearance of the electrodeposit layer on the side which is contiguous the drum.

In order to prevent adhesive and any foreign materials from entering the bath, the top of the tank 10 is preferably enclosed except where the cathode surface passes above the enclosure or flooring.

The apparatus illustrated has been used to deposit a layer of copper .00016 inch in thickness and this layer adhered to the paper and was satisfactorily stripped from the drum, by the pull-off tension being transmitted through the paper, although this thickness of deposit was not alone strong enough to withstand the requisite pull for stripping it from the cathode.

According to the best practice the electrolyte 11 will need to be circulated within the tank 10, and possibly outside the tank for renewal in event the metal shall be deposited from the electrolyte rather than from the renewable anode 13.

Depending on the type of adhesive, the thickness of the metal layer and the kind of paper, it may be sometimes desirable to use even higher temperatures than those specified but in all cases the temperature should be below that at which the paper will char and also below that temperature at which the shrinkage of the metal layer on cooling will be sufficient to fracture or break the layer either before or after stripping.

It has been found that the adhesive used is capable of setting sufficiently quickly for the stripping to occur with as little as four feet of contact between the cathode and paper. The water for washing the surface of the metal layer on the cathode after leaving the electrolyte and before reaching the pressure roll 21, is preferably sprayed on the metal layer and then caught and carried off to the sides so that it will not fall into the weaken the bath.

Some convenient form of pyrometer or thermometer is preferably connected to the applicator roll 17, the heated bath in the tank 19 and also for the re-heater 20 in order that the de-

sired accurate control of temperature may be obtained.

A large number of adhesives are available. Any suitable natural or synthetic resin such as ester gum, resin, or some of the well known materials marketed under the names of cumar (a paracoumarone-indene resin), santolite (a condensation product of formaldehyde and aromatic sulfonamides), together with an appropriate plasticizer such as tricresyl phosphate, dibutyl phthalate or others may be combined to give the following desired characteristics.

The adhesive must be capable of flowing sufficiently to allow an even and light distribution of it over the surface of the paper, but yet not so fluid as to permeate the body of the paper or other fibrous foundation in the same way that a solvent type adhesive would do, since the adhesive will be quicker setting when it is on the surface rather than extending through the fibrous foundation.

The adhesive should be capable of contacting with the metal layer in all rough spots or in all hills and valleys so that all portions of the metal layer are in contact with the adhesive and therefore all portions will be stripped from the cathode.

On cooling both before and after being stripped the metal layer shrinks or contracts whereas the heated paper takes up moisture on cooling and tends to expand with the result that the adhesive between the metal coat and paper after it has been stripped is placed under stress which requires it to be of a flexible nature in order to withstand this stress, as well as to withstand the handling and uses to which metal coated paper may be placed. This contraction of the metal coat is believed to be an important element in obtaining the tight and satisfactory application of the metal layer to the paper. Resinous adhesives of the types mentioned above may be given the requisite flexibility by the use of some of the well known plasticizers.

With rigid rotating type cathodes a quick setting adhesive is necessary on account of the limited time and space available in which to set the adhesive and strip the metal layer before the drum is cleaned and burnished. So far as is known the best adhesives to use for the rigid cathodes are flexible adhesives which set quickly on cooling. The sharper the melting point possessed by the adhesive the quicker it may set. The nature of the adhesive will depend upon operating conditions, the length of time available for the adhesive to set, etc.

One specific example of an adhesive which has been found satisfactory is a combination of a phthalic anhydride resin to give hardness to the adhesive when set, a vinyl resin to give it flexibility, and a chlorinated diphenol resin to enhance the binding or adhesive character of the material, such a particular composition having been described in my co-pending application, Ser. No. 716,504, filed March 20, 1934, for the Art of coating and laminating fabrics.

While flexible, resinous adhesives which are quick setting on cooling are believed necessary for use with a rigid rotating cathode, nevertheless where a flexible cathode for example is used a flexible adhesive may be used which is of other types, for example a flexible adhesive of a solvent type might then be appropriate because the limitations on the time available for setting of the adhesive are not so strict. The flexible cathode might be carried at commercial electrodepos-

osition speeds for a long enough time to give the adhesive whatever time is required for it to set. Resinous adhesives having a suitable plasticizer added to give them the desired flexibility may also be used when of the solvent type.

After coating paper with a thin layer of copper for example or other metal such as nickel, silver or tin, etc. another phase of this invention contemplates the electrodeposition upon the copper coated paper of a very thin layer of a weather resistant metal such as chromium, the second coat being only about .00001 inch in thickness.

To coat the metal coated paper with this second or finishing surface, the paper coated with say copper is passed onto a rigid rotating type cathode, then through a bath for chromium plating and out again, the copper coating being radially outside the paper on this chromium coating cathode.

To safeguard the paper for the chromium plating operation it is desirable to use an electrolyte of such type that it will not affect the foundation or paper which has already been coated for example, with a sulphate or kraft paper, a sulphate type electrolyte is used.

Another way in which the paper can be protected during the chromium plating operation so that it will not be injured by the electrolyte of this second bath, is to have the paper pressed so tightly against the drum that the bath will not have time to affect it except along the edges and such injured edges can then be later trimmed off. Of course where the chromium deposit of such thinness is desired the speed of the cathode may be much higher than that which has been specified for the copper coating.

Among the advantages of this invention may be mentioned the stripping of the metal layer from the cathode without the use of either a stripping knife or any oxide, sulphide or other film placed on the cathode to make the deposit layer easily removable. The tension necessary to strip the metal from the cathode is transmitted largely or at least in major portion by the flexible foundation, since metal layers much thinner than .0013 inch in thickness have been found too thin to withstand the stresses incident to commercially stripping them from a lead cathode surface. The use of plasticizers to make various resinous adhesives flexible permits the adhesive to be under the stress of an expanding foundation and a contracting metal layer.

Another advantage of the adhesives which set on cooling is that the paper and metal layer are also heated with the result that the metal layer is stretched after being applied to the paper so that it possesses a tight fit and good finish in appearance. This last advantage may, however, be present with the use of solvent type adhesives when the paper and metal are heated sufficiently to give the desired result on cooling.

Instead of the thin chromium deposit, a thin deposit of tin or silver or gold is possible.

Where the edges of a flexible cathode are trimmed, in connection with either the first or second coating, such eliminates the need of keeping the edges of the flexible cathode free from deposit within the bath. If this trimming be used with the first coat, it should of course occur before the stripping operation.

Having the paper wider than the cathode is believed to provide additional strength for stripping the edges of the deposit layers. Numerous resinous adhesives possess satisfactory dielectric characteristics to permit the metal coated paper

to be used as condensers, and paper coated under this invention is considerably cheaper than the customary foil heretofore employed in the manufacture of electric condensers.

The adhesive selected must be permanently flexible, not expensive, uniform and reasonably hard when set. An advantage of the resinous adhesives is that being plastic in their natural state, it is not necessary to introduce glycerins into the paper previous to the stripping since such adhesives naturally adhere to the paper and metal and are waterproof. These adhesives must be able to fill in pin holes resulting from faulty deposition of metal. The hot melted adhesive may be applied to the paper long prior to the use of the paper in stripping the metal layer from the cathode. In other words, the paper may be coated at the mill with this adhesive and shipped to the refinery for the stripping process. The coating of the paper with the adhesive may take place at a much higher commercial speed of operation than is possible for an electrodeposition process with the result that one coating machine may be capable of supplying a number of depositing and stripping machines. The use of the adhesives which set on cooling is considerably cheaper than the use of those of the same type which are applied with a solvent.

This invention must not be confused with the suggestions contained in the patent to Endruweit No. 676,357 dated June 11, 1901, inasmuch as the disclosure of this old patent never, so far as is known, went into practical operation, probably for a number of reasons. For one thing the stripping was not by tension applied largely through the paper.

Instead of the paper being the principal stripping agent a sulphide layer or coat was used for the purpose of making the deposit layer more easily removable, but as previously pointed out such layers were not satisfactory. Animal glue generally crystallizes and becomes too brittle on setting and does not possess the requisite flexibility for the various uses for which the paper is intended. The disclosure of this old patent is probably in operative because the deposit layer would be hard to remove from the edges of the cathode. No provision was made for either trimming the edges before stripping or having the paper wider than the metal layer to give added strength for stripping the edges. Still another objection would be the fact that the cathode became coated at least to some extent on both sides, yet an effort was made to remove the metal layer from only one side with the result that the cathode with use became thicker and less flexible.

Neither should this invention be confused with that of Cowper-Coles Patent Number 951,365 dated March 8, 1910, who contemplated stripping the deposit layer from a rigid cathode by means of a stripping knife and also by the use of films on the cathode to facilitate removal of the metal layer. The alleged stripping occurred too close to the place of contact between the gummied paper and the metal layer, there being no time interval for any setting of the adhesive to occur, whereby it should be apparent that the paper could not transmit sufficient tension through an unset adhesive.

The time or sequence in the steps of this present process at which the cleaning of the cathode side edges shall take place is necessarily before stripping whether the cleaning be performed during deposition or thereafter, and if the cleaning step is not performed during deposition it

need not necessarily be performed before the paper has been brought in contact with the cathode.

I claim:

1. The process of continuously removing a layer of electrodeposited metal from a moving cathode when the metal is so thin that it does not possess of itself enough strength to withstand the tension necessary to pull it off the cathode, which comprises pressure contacting the layer of metal on the cathode with a tensioned flexible fibrous foundation which is stronger than the metal layer and with an adhesive which is permanently flexible, uniform, and reasonably hard when set, moving the cathode with the adhering metal layer and foundation while maintaining tension on the fibrous foundation until the adhesive sets enough to permit the foundation and metal layer being pulled off together and then stripping by tension applied in major portion through the foundation to strip the metal layer from the cathode without the aid of any stripping knife or chemical film being applied between the cathode and metal layer to facilitate its removal.
2. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises feeding a flexible paper, heating a thermoplastic adhesive to an elevated temperature, applying said heated adhesive between the paper and metal layer on the cathode, pressure contacting the paper and metal with the adhesive therebetween while hot and tacky, moving the paper and metal layer with the cathode until the adhesive has at least partially set, and stripping the paper and metal layer from the cathode.
3. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises feeding a flexible fibrous foundation, heating to an elevated temperature a thermoplastic resinous adhesive having a sharp melting point, applying said heated adhesive between the foundation and metal layer on the cathode, pressure contacting the foundation and metal layer with the adhesive therebetween while hot and tacky, moving the foundation and metal layer with the cathode until the adhesive has at least partially set thus solidifying the adhesive sufficiently and quickly enough to prevent its substantial penetration of the foundation, and stripping the foundation and metal layer from the cathode.
4. The process of continuously removing a layer of electrodeposited metal from a moving cathode when the metal is so thin that it does not possess of itself enough strength to withstand the tension necessary to pull it off the cathode which comprises feeding a flexible paper, heating a thermoplastic adhesive to an elevated temperature, applying said heated adhesive between the paper and metal layer on the cathode, pressure contacting the paper and metal with the adhesive therebetween while hot and tacky, moving the paper and metal layer with the cathode until the adhesive has at least partially set, and applying tension in major portion through the paper to strip the metal layer from the cathode.
5. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises feeding a flexible fibrous foundation, heating to an elevated temperature of about 300° F. a thermoplastic resinous adhesive having a sharp melting point, applying said heated adhesive between the foundation and metal layer on the cathode, pressure contacting the foundation and metal layer with the adhesive therebetween while hot and tacky, moving the foundation and metal layer with the cathode until the adhesive has at least partially set thus solidifying the adhesive sufficiently and quickly enough to prevent its substantial penetration of the foundation, and stripping the foundation and metal layer from the cathode.
6. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises applying a flexible thermoplastic resinous adhesive to a substantially continuous strip of flexible paper while hot and tacky, feeding the paper, pressure contacting the paper and metal layer with said adhesive therebetween, reheating the adhesive on the paper to increase its tackiness just before said pressure contacting, moving the paper and metal layer with the cathode until the adhesive has at least partially set, and stripping the paper and metal layer from the cathode.
7. The process of continuously removing a layer of electrodeposited metal from a moving rigid cathode which comprises feeding a flexible fibrous foundation, heating to an elevated temperature a thermoplastic resinous adhesive having a sharp melting point, applying said heated adhesive between the foundation and metal layer on the cathode, pressure contacting the foundation and metal layer with the adhesive therebetween while hot and tacky, moving the foundation and metal layer with the cathode until the adhesive has at least partially set thus solidifying the adhesive sufficiently and quickly enough to prevent its substantial penetration of the foundation, and stripping the foundation and metal layer from the cathode.
8. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises feeding a flexible paper, heating a thermoplastic adhesive to an elevated temperature, applying said heated adhesive between the paper and metal layer on the cathode, pressure contacting the paper and metal with the adhesive therebetween while hot and tacky and with the paper extending laterally beyond the side edges of the metal layer, moving the paper and metal layer with the cathode until the adhesive has at least partially set, and stripping the paper and metal layer from the cathode.
9. The process of continuously removing a layer of electrodeposited metal from a moving cathode which comprises feeding a flexible paper, heating a thermoplastic adhesive to an elevated temperature, applying said heated adhesive between the paper and metal layer on the cathode, pressure contacting the paper and metal with the adhesive therebetween while hot and tacky, moving the paper and metal layer with the cathode until the adhesive has at least partially set, stripping the paper and metal layer from the cathode, and subsequently applying a thinner layer of weather resistant electrodeposited metal to the previous metal layer without injuring the paper by the electrolyte in such subsequent electrodeposition.

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