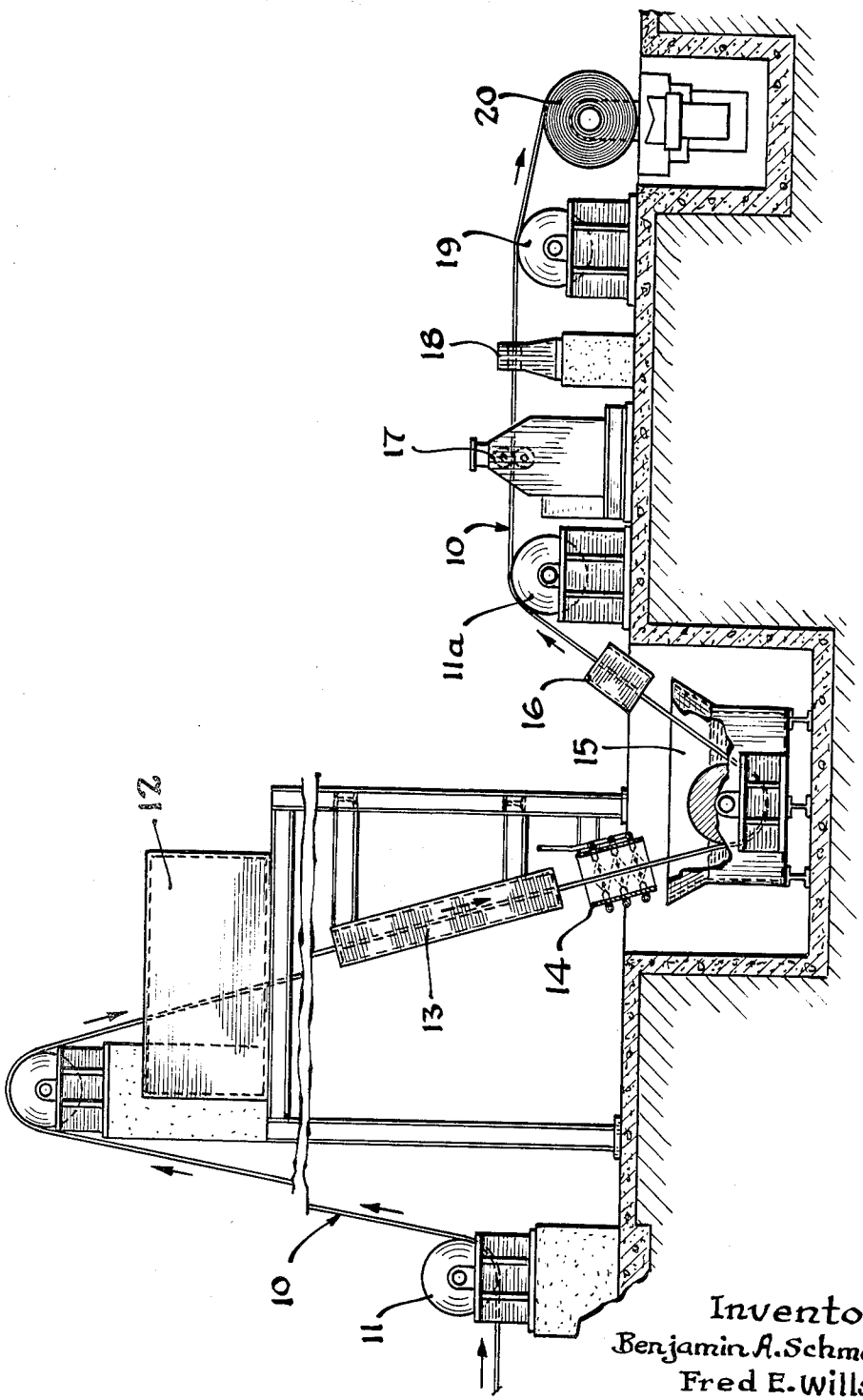
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Inventors
Benjamin A. Schmetterer
Fred E. Wills

By Davis, Lindsey, Hibben & Noyes
Attorneys

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COATING WITH A POLYAMIDE-EPOXY RESIN

Benjamin A. Schmetterer, 4165 S. Emerald Ave., Chicago, Ill., and Fred E. Wills, Gary, Ind. (% Inland Steel Co., East Chicago, Ind.)

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The present invention relates generally to coating surfaces of an article and more particularly to an improved process and material for providing an organic film coating on a surface of an article, such as a galvanized metal strip or sheet, and to the organic film coating and coated article produced.

Most of the metals widely used in commerce are subject to attack on exposure to the atmosphere or other corrosive fluids. The phenomenon of corrosion of "white rust" is frequently encountered in the building trades where it is common practice to expose sheets of metal to corrosive atmospheric conditions. Ferrous metal surfaces, for example, are readily oxidized or corroded. Likewise, many of the non-ferrous metals, such as tin, zinc, aluminum, and tin-coated, galvanized or aluminum coated ferrous metals, must be protected against "white rust" forming on the surface thereof.

Many ways and means have been employed to protect metal surfaces against corrosion and "white rust." This is usually solved by covering the surface of the metal with a protective film. Thus, for example, galvanized metal sheets have been covered by a protective film of oil, wax, varnish, or subjected to a chemical treatment, such as contacting the surface thereof with a chromic acid solution. However, none of these protective treatments achieve all of the desired results, such as being economical to apply, highly protective to the metal surface, free of objectionable coloration on the metal surface, capable of being painted without requiring removal of the protective coating, and capable of being highly decorative.

A protective coating for metals which possesses the foregoing desirable attributes is a polyamide-epoxy resinous reaction product, but heretofore polyamide-epoxy resin coatings have been too costly for general usage in the buiding trades, for example, which uses large quantities of galvanized steel sheets, aluminum or aluminum coated ferrous metal sheets. The application of a polyamide-epoxy resin coating has been heretofore limited to the relatively expensive low-speed, small volume treatment of metal strips after the fabrication of the strips has been completed by the mill. None of the methods of applying a polyamide-epoxy resin coating or other organic protective coating has heretofore been suitable for applying a protective and/or decorative organic coating of the instant type to a metal strip moving at a relatively high rate of speed and within the space limitations imposed in continuous strip mill "in-line" operation, such as a continuous galvanizing line or continuous tin plating line.

It is, therefore, an important object of the present invention to provide a method and materials which are capable of being used to form an organic coating of a polyamide-epoxy resin composition on a surface of a moving strip of metal in a strip mill "in-line" operation.

It is a further object of the present invention to provide a method and materials which are capable of being used to form a polyamide-epoxy resin coating on a galvanized steel strip in a continuous galvanizing "in-line" operation.

It is also an important object of the present invention to provide method and materials which are capable of being used to form an improved fully cured protective coating of polyamide-epoxy resin composition on

a metal surface within a period of about 2 to 4 seconds after contacting the metal with an uncured fluid resin film.

It is still a further object of the present invention to provide a method and materials which are capable of being used to rapidly and economically form on a surface of an article a fully cured polyamide-epoxy resin coating having good protective and decorative properties.

It is still another object of the present invention to provide a method and materials which are capable of being used to produce a polyamide-epoxy resin coating on a metal surface which is highly suited for retaining thereon a finish or top coating of paint, lacquer or the like.

It is also an object of the present invention to provide a novel method of producing a solution of a polyamide resinous material and an epoxy resinous material suitable for spray application to a metal surface and adapted to be rapidly cured at high temperatures.

Another object of the present invention is to provide a stable solution of a polyamide resin in a halogenated hydrocarbon solvent.

Still another object of the present invention is to provide a novel polyamide-epoxy resin composition capable of being used for the production of a rapidly curable polyamide-epoxy resin reaction product.

Other objects of the present invention will be apparent from the detailed description and claims to follow when read in conjunction with an accompanying drawing wherein there is shown a schematic representation of an arrangement of apparatus suitable for use in the the practice of the present invention.

It has been discovered that a metal surface of steel, zinc, tin or aluminum or a ferrous metal surface coated with zinc, aluminum, or tin in the form of sheets, strips or shaped articles and other articles, such as ceramic articles, can be provided with a protective and/or decorative fully-cured polyamide-epoxy resin reaction product coating within a few seconds of the application of an uncured resin film on the surface of an article by applying a halogenated hydrocarbon solvent solution of a polyamide resinous material and an epoxy resinous material to the metal surface under controlled conditions. And, while polyamide-epoxy resins dissolved in various organic solvents have been previously applied to a variety of articles, none of the solvent solutions heretofore used have been adapted for use in a process which forms a fully cured protective coating on a metal surface within a few seconds of the application thereof to the surface of an article.

It has now been unexpectedly found that a halogenated lower aliphatic hydrocarbon solvent, preferably containing by weight in excess of 50 percent methylene chloride, is capable of solubilizing both an epoxy resinous material containing free epoxy groups and a polyamide resinous material containing free amine groups, and that the resulting resin solution possesses the necessary volatility and non-flammability required for the "in-line" application thereof to a metal strip being produced on continuous strip mill line operation. Other chlorinated hydrocarbon solvents which can be used with methylene chloride are perchloroethylene, trichlorethylene, trichlorethane and tetrachlorethane.

To enable a halogenated hydrocarbon solvent, particularly those containing methylene chloride, to be effectively used as the solubilizing agent for the polyamide resin or a mixture of polyamide resin and an epoxy resin, it was found desirable to stabilize the chlorinated hydrocarbon solvent solution containing the polyamide resin to prevent the said solution, and particularly the polyamide resin component thereof rapidly forming a

highly viscous or gelatinous mass before the resin solution could be applied as a thin continuous film. Thus, a further important aspect of the present invention which for the first time makes possible the large scale commercial strip mill "in-line" application of a coating of polyamide-epoxy resin reaction product to a metal surface resides in the discovery of a means for stabilizing the chlorinated hydrocarbon solvent solution containing a polyamide resin.

It was found possible to stabilize a methylene chloride-polyamide resin solution, for example, by including therein a sufficient quantity of an alkaline compound which is soluble in the halgonated hydrocarbon solvent solution and which is capable of functioning as a buffering agent to maintain the pH of the halogenated hydrocarbon solvent solution at about the normal pH of the said polyamide resin dissolved therein. When thus buffered the useful life of the polyamide containing resin solution is prolonged appreciably to permit the application of a thin continuous film thereof in combination with an epoxy resin to a metal strip or other article before appreciable polymerization takes place and without interfering with the rapid curing of the polyamide-epoxy resin mixture. Morevore, there are definite indications that at the highly elevated resin curing temperature employed in the present invention, the methylene chloride serves as a catalyst to promote the rate of curing of the resin mixture by means of the catalytic effect of the high temperature decomposition products of the methylene chloride.

As an example of an alkaline compound which functions as a buffering agent in the halogenated hydrocarbon solvent system containing a polyamide resin, one can employ basic organic nitrogen compounds, including the lower aliphatic amines, such as n-butylamine or n-hexylamine. Also, other alkyl amines or cyclic amines can be used. In every instance, however, the amine used should be less volatile than the halogenated hydrocarbon solvent. Thus, if trichloroethylene having a boiling point of about 189° F. were used in the solvent, the amine used as the buffering agent should have a boiling point of about 250° F., or above. A sufficient amount of the buffering agent is added to the halogenated hydrocarbon solution containing the polyamide resin to raise the pH thereof to substantially the pH of the particular polyamide resin dissolved in said hydrocarbon solvents. The pH of the resulting buffered solutions are generally between about pH 9 and 9.5. It will be readily apparent, however, that the amount of buffering agent employed will depend on the relative amounts of polyamide present, its concentration and the properties of the particular chlorinated hydrocarbon solvent employed.

In preparing a halogenated hydrocarbon solvent solution of a polyamide resin and an epoxy resin suitable for application to a metal surface and which preferably contains between 5% and 35% by weight of the nonvolatile resins, the polyamide resin and the epoxy resins are first individually dissolved in a halogenated hydrocarbon solvent and are maintained out of contact with each other until shortly before use, as the polyamide resin and the epoxy resin chemically react with each other and therefore only have a limited shelf life after mixing.

A halognated hydrocarbon solvent solution of a polyamide resin is prepared by first charging a suitable mixing apparatus with the required amount of halogenated hydrocarbon solvent for dissolving the polyamide resin and then slowly adding the polyamide resin which is preferably heated so that it is readily pourable. A violent boiling action takes place and careful control must be used to maintain the temperature of the solvent solutions near its boiling point. The mixing apparatus, such as a kinetic mill, should be equipped with a reflux condenser. After all of the polyamide resin has been dissolved in the halogenated hydrocarbon solvent, the solution is cooled to a temperature below the boiling point of the buffering agent to be added and the buffering agent is dissolved in the solution to form a homogeneous mixture. The polyamide resin concentration in the halogenated hydrocarbon solution can be as high as 65% by weight but preferably comprises not substantially in excess of about 50% by weight. When higher resin concentrations are initially prepared, these can be readily reduced to a 50% concentration by mixing therewith additional halogenated hydrocarbon solvent. When prepared in the above manner in about a 50% concentration, the halogenated hydrocarbon solvent solution of the polyamide resin is stable for a prolonged period and can be readily mixed with a solution of epoxy resin in the halogenated hydrocarbon solvent shortly before application to a metal surface.

A halogenated hydrocarbon solution of an epoxy resin can be readily prepared in any suitable mixing apparatus, such as a kinetic mill equipped with a water cooled reflux condenser, by adding the halogenated hydrocarbon solvent in the required amount and then adding the solid epoxy resin to the halogenated solvent. The resin is mixed with the solvent until a uniform solution is formed.

The polyamide resinous materials which can be used for preparing the foregoing solvent solutions are, in general, those polyamides of carboxylic acids which are polymers of polyene fatty acids and their esters. Resins of this general type are disclosed in T. F. Bradley's U.S. Patent No. 2,379,413. Typical of these polyamides are those made with polymerized polyene fatty acids and ethylene diamine, although other amines, such as methylamine, propylamine, cyclohexylamine and dodecylamine can be used. In general, resins having amine numbers within a range of 50–200 are preferred for the present purposes, although other resins can also be used where special properties are desired.

The polymeric fatty acids preferably employed in preparing the polyamides are those resulting from the polymerization of the polyene or drying and semi-drying oils, or the free acids or simple aliphatic alcohol esters of such acids. Suitable drying or semi-drying oils include soybean, linseed, tung, perilla, oiticia, cottonseed, corn, tall, sunflower, safflower, dehydrated castor oil and the like from which is derived α-eleostearic acid; β-eleostearic acid; linolenic acid; 9,11-octadecadienic acid; and 9,12-octadecadienic acid. In the polymerization process for the preparation of the polymeric fat acids, the fatty acids with sufficient double bond functionality combine, for the most part probably by a Diels-Alder mechanism, to provide a mixture of dibasic and higher polymeric acids. The acids with insufficient functionality to react remain as monomers and may be wholly or partially removed, for example by distillation. The residue after distillation consists of the desired polymeric polyene fatty acids and this mixture is used for the preparation of the polyamide resin. In place of this method of polymerization, any other method of polymerization may be employed, whether the resultant polymer possesses residual unsaturation or not. The polymeric fatty acids used in the prepartion of the polyamine usually contains a substantial portion of dimeric acids and a quantity of higher polymeric acids, and some residual monomer.

The amidification reaction may be carried out under the usual conditions employed for this purpose. Polyamides of this type generally have molecular weights varying from 1,000–10,000 and are usually resistant to the corrosive action of water, alkali, acids, oils, greases and organic solvents. The melting points vary, depending upon the reactants and the reaction conditions.

In some instances it is also desirable to include with the polymerized polyene fatty acid in the amidification reaction an ordinary straight chain dicarboxylic acid such as adipic acid, sebacic acid, pimelic acid, or the like. In this way polyamide resins having increased flexibility and the like properties can be produced.

The present invention is applicable to epoxy resins in general. These epoxy resins are complex polymeric re-

action products of polyhydric phenols with polyfunctional halohydrins, such as epichlorhydrin and glycerol dichlorhydrin. Usually the difunctional chlorhydrin is used in proportions in excess of that equivalent to the polyhydric phenol and less than that which is twice the equivalent amount. The reaction is carried out in the presence of caustic alkali which is usually employed in at least the quantity necessary to combine with the halogen liberated from the halohydrin, and usually is employed in excess. The products obtained may contain terminal epoxy groups or terminal epoxy groups and terminal primary hydroxyl groups. In the complex reaction mixtures the terminal epoxy groups are generally in excess of the terminal primary hydroxyl groups. Typical polyhydric phenols include resorcinal, and various bisphenols resulting from the condensation of phenol with aldehyde, acetone, methyl ethyl ketone, and the like. Resins of this type are disclosed in Greenlee Patent No. 2,585,115 and these resins are useful in the present invention.

There is a wide variation in the relative proportions of the polyamide resinous material and the epoxy resinous material which can be employed. Thus, while the polyamide resin can be employed as the major constituent with a minor amount of epoxy resin, best results have been obtained with compositions varying from (by wt.) about 80% epoxy resin and 20% of polyamide resin to about 50% epoxy resin and 50% polyamide resin. When 25% of the polyamide is used with 75% of the epoxy resin, for example, a cured film material is obtained which is both hard and tough and which is well suited for coating metal strips. Other resin proportions give useful protective and/or decorative films, and the properties thereof will vary with the particular proportions used.

In order to impart improved decorative properties to the polyamide-epoxy resin coating pigments can be added to the polyamide resin solution or to the epoxy resin solution. Thus, for example, pigments including phthalo blue, phthalo green, benzidine yellow, ferric hydrate, or titanium oxide can be admixed with the epoxy resin solution in a kinetic mill during the preparation of the epoxy halogenated hydrocarbon solution. Also, if improved corrosion resistance is desired, a suitable chromate compound, such as zinc chromate, can be admixed with the resin solution.

The method of applying the buffered halogenated hydrocarbon solution of a polyamide resin-epoxy resin mixture will depend somewhat on the article being coated. Thus, a formed article can be either dip coated or spray coated. If a dip coating method is used for coating either a formed article or a strip, it is advisable to refrigerate the coating solution where the solvent is primarily methylene chloride or other relatively highly volatile solvent. While a dip coating method or even a curtain coating method could be used to apply the instant resin solution to a moving metal strip, it has been found that the resin solutions of the present invention can best be applied to a surface of a moving strip of metal by means of a hydraulic or airless spray application. Thus, whereas the use of high pressure gases which mix with the resin solution to disperse the resin solution has been found to be entirely impractical, very good results are achieved by using an hydraulic or airless spray process for applying a thin continuous film of the resin solution.

By using an hydraulic spray process or an airless spray process a thin continuous organic film coating of said polyamide-epoxy resin solution having a uniform and controlled thickness can be applied to the surface of an article, including a continuously moving strip of metal. It has been found that coatings of from about .2 mil to 2.0 mils (cured thickness) can be very rapidly and conveniently applied. A cured resin coating of the present invention which has a thickness of at least 0.5 mil provides substantial protection against corrosion or "white rust" formation. The coatings can be conveniently formed to any desired thickness by controlling the concentration of the resin solids in the solvent solution and the type and number of spray nozzles used. The pigmented coatings are also highly decorative.

In applying a buffered halogenated hydrocarbon solution of a polyamide resin and an epoxy resin to a moving strip of metal, such as a galvanized steel strip on a continuous galvanizing line, it has been found highly desirable to spray the halogenated hydrocarbon solution of polyamide resin and epoxy resin onto the clean, dry strip soon after the strip leaves the zinc coating bath before the surface becomes contaminated with grease or oil. It is also possible to pretreat the galvanized metal strip to increase the corrosion resistance thereof by means of a conventional passivation treatment, such as a chromic acid dip, before the polyamide-epoxy resin solution is sprayed onto the moving metal strip. The latter procedure is particularly desirable where only a very thin protective coating or resin is applied and where the resin coating alone is insufficient to completely protect the metal surface against the contemplated corrosive conditions to which the metal will be exposed. When a thicker coating of the resin solution is applied to the strip, however, these is no necessity for using a preliminary passivation treatment on the galvanized strip, as the resin coating over the galvanized surface provides the required protection against corrosion and "white rust."

The temperature of the galvanized strip at the time the resin solution is applied can vary considerably and with certain resins and solvent solutions the strip can be heated to a relatively high temperature or allowed to remain at a relatively high temperature when the resin coating is applied. Generally, however, the temperature of the metal strip is maintained between about 75° and 150° F., with the preferred temperature thereof being about 100° and 130° F.

When the halogenated hydrocarbon solvent solution of the polyamide and epoxy resins is applied "in-line" to a moving strip of metal by spraying, it is necessary that the strip have a substantially constant linear speed at the time the solution of resins is sprayed thereon so that the thickness of the resin film applied is uniform and can be accurately controlled. A variation of line speed of about 10 to 15 feet per minute where the average line speed is approximately 200 feet per minute is not a serious variation, but substantially greater variations in line speed should be avoided.

After the metal strip has been coated with a uniform film of polyamide-epoxy resin dissolved in a halogenated hydrocarbon solvent, as herein described, the strip is immediately passed through a curing chamber, such as a gas heated oven or an induction heated furnace where the resin coating is rapidly heated for a very short period to effect complete removal of the solvent and completion of the reaction between the polyamide resin and the epoxy resin, whereby the resin film is completely cured to produce an insoluble and infusible resin coating. The temperature to which the coating is exposed in the preferred embodiment can vary between 1000° to 2000° F., with best results being obtained with temperatures in the curing chamber between about 1500° and 1700° F. and with the resin film being exposed to said temperatures for only a few seconds (i.e., 3 to 5 seconds). With the temperature of the curing chamber about 1000° F. the coating is cured within a period of about 45 seconds and at a temperature of 2000° F. the resin coating is completely cured within a period of about 2 seconds. When coating a metal strap "in-line" the curing chamber is preferably maintained at a temperature of about 1500° F. and the strip is exposed to the latter temperature for a period of about 4 or 5 seconds, after which the resin coating is completely cured. It will be apparent that the temperature of the curing chamber can be selective to correlate with the linear speed at which a particular strip is moving and the length of a particular curing chamber. Thus, if a strip were moving at a high linear speed, it would not be practical to employ a curing chamber having a tempera-

ture of only 1000° F., since an extremely long curing chamber would be required. If only a very limited space were available for a curing chamber, the temperature within the curing chamber would have to be relatively high with the strip moving therethrough at a relatively high rate.

It has been further observed that when the temperature of the curing chamber is maintained between about 1000° and 2000° F., the rate of curing of the resin reaction products proceeds much faster than at temperatures appreciably lower than 1000° F. The rate of reaction observed within the preferred temperature range of 1000° and 2000° F., is not that which is predictable from the standard relationship between temperature and rate of reaction. It appears that there is a catalytic reaction taking place and it is postulated that the substantially increased rate of curing observed is due to the presence of the halogenated hydrocarbon solvent solution or more particularly the decomposition products of methylene chloride formed at the said elevated temperatures.

A further advantage achieved by the use of the elevated resin-curing temperature for only an extremely short period is that the strip or article being treated is exposed to heat for such a relatively short period that the strip or article itself does not become heated to a very high temperature. Thus, it is possible to avoid melting a protective undercoating of a relatively low melting point metal or other nonmetallic coating, as well as avoiding damaging soldered connections or the like.

In the preferred method of coating a strip of metal in accordance with the present invention the resin coated strip is subjected to a quenching treatment immediately after the strip leaves the heated chamber to rapidly cool the resin coating to room temperature. It has been found convenient to effect the quenching by spraying cool water onto the resin surface and immersing the resin coated strip or article in a cool water bath. Water having a temperature of about 70° F. or below has been found suitable for quenching the resin coating.

The quenching of the resin coated strip as it leaves the heated curing chamber has in certain instances been found to impart to the resin coating an unexpected property of being appreciably more receptive to painting or lacquering than the same polyamide-epoxy resin coating which was not subjected to the quenching treatment. Thus, the quenched resin coating was found to be much more adherent to paints and lacquers. Also a quenched resin coated metal sheet having a painted or lacquered coating thereover which normally cracks when the supporting metal sheet is formed or drawn could be formed and drawn without damaging the paint or lacquer surface. The same resin coated sheet which is not subjected to a quenching treatment could not be drawn or formed without damaging the painted or lacquered surface coating. It is therefore postulated that the rapid cooling of the resin coating produces a novel crystal structure in the resin coating which substantially improves the ability of the resin coating to retain a surface finish coating applied thereover.

As shown in the accompanying drawing illustrating one arrangement of apparatus suitable for "in-line" application of the instant resin solvent solution to a metal strip, an elongated galvanized steel strip **10** which is passed between power rollers such as **11**, **11***a*, to maintain the strip moving at a constant linear speed is passed through an enclosed airless or hydraulic spray chamber **12** where the polyamide-epoxy resin solvent solution of the present invention is applied. The strip **10** with a thin film of the resin solution applied to at least one surface thereof is next conveyed to a heated chamber or furnace **13** which is maintained at a temperature between 1000° and 2000° F., wherein the resin solution is fully cured within a matter of seconds. Thereafter, the strip **10** is passed through a preliminary quenching chamber **14** wherein cool water is sprayed on the resin coating and then the strip is passed through a water quenching tank **15** to complete the rapid cooling of the coated strip **10** to room temperature. The strip **10** is then passed through a dryer **16** over a roller **11***a*, between conventional pinch rolls **17**, over roll **19**, and finally is wound on reel **20**, or if desired, the resin coated strip can be cut by shears **18** into suitable lengths and stacked.

While the coating apparatus described hereinabove can be conveniently placed following the metal coating apparatus in a continuous metal coating line, the above described apparatus can also be used in any portion of a metal strip forming or strip treating line wherein the strip is moving at a substantially constant speed and after the surface of the strip has been freed of surface contamination.

In order to further illustrate the process of the present invention, the following specific examples are set forth without, however, limiting the invention to the specific materials and conditions employed.

Example I

A clean hot-dipped galvanized steel strip travelling along a continuous galvanized line at a substantially constant linear speed of about 180 feet per minute and having a temperature of about 130° F. is conducted through an airless spray chamber wherein the surface of the strip is sprayed by airless spray apparatus with a polyamide-epoxy resin methylene chloride solvent solution.

The polyamide-epoxy resin methylene chloride solvent solution is prepared by admixing a n-butylamine buffered polyamide resin solution in methylene chloride solvent and an epoxy resin solution in methylene chloride solvent in a ratio sufficient to form a solution having one part polyamide resin and one part epoxy resin on a weight basis and having a total polyamide-epoxy resin content of 10% on a weight basis.

The polyamide resinous material used herein is produced by reacting a polyamide and dibasic acid in accordance with the teaching of U.S. Patent No. 2,379,413 with the resultant polyamide resin having an amine value of between about 83–93 and a Brookfield viscosity at 150° C. of 7–12 poises. A polyamide resin having the above properties is sold under the trade name "Versamid 100" by General Mills, Inc.

The buffered polyamide resin methylene chloride solution is prepared by adding 100 pounds of "Versamid 100" slowly to 100 pounds of methylene chloride in a kinetic mill provided with a water cooled reflux condenser. After all the "Versamid 100" has been mixed with the methylene chloride to form a homogeneous solution, the solution is cooled to a temperature of about 70° F., and 4 pounds of normal butylamine having a boiling point of about 172° F. is uniformly mixed with the methylene chloride solution to provide a solution with a pH of about 9 to 9.5.

Epoxy resinous material employed in the preparation of the epoxy methylene chloride solution is a bisphenyl-epichlorhydryn reaction product prepared, for example, as in U.S. Patent No. 2,521,911, said epoxy resin preferably having epoxide equivalent of about 500–550. An epoxy resin having the above properties is sold under the trade name "GenEpoxy 525" by General Mills, Inc.

The epoxy-methylene chloride solvent solution is prepared by adding 100 pounds of "GenEpoxy 525" to 100 pounds methylene chloride in a kinetic mill equipped with a water cooled reflux condenser and stirred until a uniform solution is formed. In the epoxy resin solution there is also preferably dispersed phthalo blue coloring in a proportion of 50 grams per gallon of epoxy solution.

The above polyamide resin methylene chloride solvent solution and the above epoxy methylene chloride solvent solution are mixed with 600 pounds of methylene chloride to form a homogeneous solution containing 20% non-volatile resinous matter prior to application of the

solution to the galvanized strip. Thereafter the methylene chloride solution of the resins prepared in the foregoing manner is, preferably within two days, sprayed onto the galvanized strip as it passes through the spray chamber by means of airless spray coating equipment. Suitable airless spray coating equipment is manufactured by the "Nordson Corporation," Amherst, Ohio. The airless spray apparatus is preferably of the reciprocable type with spray nozzles capable of applying .2 gallon per minute per nozzle of atomized resin solution in a pattern having a width of 10 inches when the spray nozzle is maintained at a distance of about 7.5 inches from the galvanized strip and when operated at a pressure of about 600 pounds per square inch. A continuous resin film having a thickness when cured of between 0.75 and 1.0 mil is formed.

The galvanized strip having a thin film of polyamide-epoxy resin composition thereon is immediately passed through a heated curing chamber maintained at a temperature of about 1500–1600° F. The curing chamber has a length of about 6 feet so that the coating strip is maintained within the heated chamber for a period of about 3 to 4 seconds. During the passage of the strip through the curing chamber the polyamide resin reacts chemically with the epoxy resin to form a thermo setting resin reaction product and the volatile components of the resin solution are removed.

The galvanized strip with the cured polyamide-epoxy resin reaction product coating thereon is subjected immediately after it emerges from the curing chamber to a water quenching treatment comprising spraying thereon cool water having a maximum temperature of about 70° F. and then immediately immersing the moving strip in a cool water bath having the temperature thereof maintained at about 70° F. The resin coating is thereby quickly brought to room temperature and can be cooled or cut and stacked, if desired. When the strips are to be held for prolonged periods under high humidity conditions, it may be desirable to use an anti-blocking agent, such as a silicone, to prevent adjacent surfaces adhering to each other.

The polyamide-epoxy resin reaction product coating produced in the above manner provides a firmly adherent protective film on the galvanized surface of the said strip which is capable of being drawn and formed without being damaged, as evidenced by its ability to pass the Pittsburgh Lock Seam test, the Bend Seam test, the Olsen Button test, the G.E. Impact Flexibility test and the corrugation test. The resin coating also provides the metal surface with good protection against "white rust" formation or corrosion, as evidenced by the ability of the said resin coated strip to pass the wet pack test (40-hour stack test). This test is one where coated panels are sprayed with a fine mist of distilled water, placed in stack form and weighted down so that total surface contact is obtained. This stack is then put into a bell jar where an atmosphere of 100% relative humidity is maintained. The bell jar is placed in an oven where temperature is maintained at 118° F.±2. At the end of 40 hours the stack of samples are removed from the oven and bell jar, separated, dried and inspected. The degree of white rust is calculated visually and recorded.

The resin coated products of the present invention exhibit outstanding paintability to a wide variety of commercially available industrial and trade sales finish coating materials. Moreover, the resin coating imparts formability and ductility to these coatings where normally the finish coatings would not exhibit the aforementioned characteristics when applied to a galvanized surface. As an example of enhancement of the foregoing qualities of a conventional top coating, the application of a vinyl chloride finish over a resin-coated galvanized strip in accordance with the foregoing specific example of the present invention enables the vinyl-coated strip to pass the Pittsburgh Lock Seam test, the Bend Seam test, the Olsen Button test, the G.E. Impact Felixibility test and the corrugation test; whereas the galvanized strip with the same vinyl chloride finish but without the resin coating fails to pass all of the above tests. In addition, the above vinyl chloride resin-coated galvanized strip passes the Standard Weatherometer test (1,000 hours) and the Salt Spray test (250 hours).

Example 2

A buffered methylene chloride solution of polyamide and epoxy resins is prepared as in Example 1, except that the concentration of the nonvolatile resins therein is adjusted to a concentration of 5% by weight of the final solution. The galvanized strip differs from that used in Example 1 by having its surface pre-treated with a standard chromic acid solution to increase resistance thereof to "white rust" formation. The solution prepared in the above manner is continuously sprayed onto the pre-treated galvanized steel strip moving at a constant speed of about 150 feet per minute in the same manner described in Example 1. The resin coated strip is then cured and water-quenched as in Example 1. The resulting resin-coated galvanized strip has a cured resin film formed thereon having a thickness of about 0.5 mil and exhibits good resistance to white rust formation and corrosion during normal warehouse storage.

Example 3

In accordance with the procedure of Example 1, a solution of 250 pounds of polyamide resin "Versamid 100," 250 pounds of a mixed chlorinated hydrocarbon solvent solution comprising 2 parts (by weight) methylene chloride, 1 part 1-trichloroethane and 1 part perchloroethylene with 24 pounds of n-hexylamine added as a buffering agent is prepared, and a solution of 750 pounds of epoxy resin "GenEpoxy 525" in 750 pounds of said halogenated solvent solution is also prepared. Shortly before use the buffered chlorinated hydrocarbon solvent solution of polyamide resin and the said solvent solution of epoxy resin are mixed with a sufficient quantity of said mixed chlorinated hydrocarbon solvent (about 850 lbs.) to make the nonvolatile resins dissolved therein comprise about 35% by weight of the final solution.

An aluminum coated article which is suspended on an endless conveyor line is dipped in a refrigerated bath composed of the above solution of resins. The coated article is then conveyed through a heated curing chamber having a temperature of about 1200° F. within a period of about 30 seconds. Thereafter the article is quenched in a cool water bath to quickly bring the resin coating to room temperature. A firmly adherent tough resin coating is formed on the aluminum coated article. If desired, a finish coating of a vinyl resin material can be applied over the resin coating by any of the conventional methods.

When the resin coated articles are not to be painted or otherwise treated with a finish coating and do not have to be handled or stacked soon after leaving the curing chamber, the water-quenching treatment can be omitted. However, since the quenching step also appears to improve and enhance the qualities of the resin coating, it is preferable to quench the dip-coated article in a cool water bath, as in Example 1.

Although there has been shown in the drawing and described above a preferred embodiment of the present invention, it is to be understood that changes and modifications may be resorted to without departing from the spirit and scope of the appended claims.

We claim:

1. A process of coating a surface of an article with an organic resin which comprises; applying to a surface of an article a continuous film of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups dissolved in a halogenated hydrocarbon solvent containing at least about 50 percent by weight

methylene chloride, said resinous materials being present in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material, and exposing said continuous film of resinous materials on said surface to a temperature of between about 1000° F. and 2000° F. for a period of between about 45 seconds and 2 seconds to effect substantially immediate and complete curing of said resinous materials.

2. A process of providing a surface of an article with an organic resin coating which comprises; applying to a surface of an article a continuous film of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups dissolved in a halogenated hydrocarbon solvent comprising at least 50 percent by weight methylene chloride, said solution having dissolved therein as a buffering agent an amine which has a boiling point higher than the boiling point of said solvent, said resinous materials being present in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material, exposing said film on said surface to a temperature between about 2000° F. to 1000° F. for a period of between about 2 seconds and 45 seconds to form substantially immediately a fully cured resin coating.

3. A process as in claim 2, wherein said amine is a lower aliphatic amine.

4. A process as in claim 2, wherein said amine is n-butylamine.

5. A process as in claim 2, wherein said amine is n-hexylamine.

6. A process as in claim 2, wherein said amine is a cyclic amine.

7. A process of providing a metal surface with a thin continuous resin coating which comprises; applying to the metal surface a substantially uniform fluid of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups dissolved in a halogenated hydrocarbon solvent comprised of at least 50% by weight methylene chloride, said resinous materials being present in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material, and exposing said fluid film on said metal surface to a temperature between about 1000° F. to 2000° F. to effect substantially immediate and complete curing of said fluid film of said resinous materials.

8. A process of providing a strip of metal on at least one side thereof with a thin continuous coating of organic resin which comprises; continuously applying to at least one side of a strip of metal moving in a continuous processing line at a substantially constant linear speed a substantially uniform fluid film of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups dissolved in a halogenated hydrocarbon solvent comprising at least 50 percent by weight methylene chloride and having dissolved in said solvent as a buffering agent an amine having a boiling point higher than the boiling point of said solvent, said resinous materials being present in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material, continuously exposing said fluid film on said strip to a temperature between about 1000° F to 2000° F. to effect substantially immediate and complete curing of said fluid film, and continuously contacting said cured resin film with a cooling fluid to rapidly cool said film to about room temperature; whereby a firmly adherent fully cured polyamide-epoxy resin coating is continuously formed in-line on said strip of metal.

9. A process as in claim 8, wherein said amine is a lower aliphatic amine.

10. A process as in claim 8, wherein said amine is n-hexylamine.

11. A process as in claim 8, wherein said amine is a cyclic amine.

12. A process as in claim 8 wherein said halogenated hydrocarbon solvent is methylene chloride.

13. A process as in claim 8 wherein said amine is n-butylamine.

14. A process of providing a strip of metal with a thin continuous coating of an organic resin which comprises; continuously applying to at least one side of a metal strip moving in a continuous processing line at a substantially constant speed a uniform fluid film of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups dissolved in the halogenated hydrocarbon solvent having a major proportion thereof composed of methylene chloride and said resinous materials being present in a proportion of about one to four parts by weight of said epoxy resinous material to about one part by weight of said polyamide resinous material, said solution having dissolved therein as a buffering agent an amine having a boiling point higher than said solvent, exposing said fluid film on said strip to a temperature between about 1500° F. and 1700° F. for a period about 3 to 5 seconds to effect substantially immediate and complete curing of said film, and rapidly cooling said film and said strip to about room temperature by contacting with a cooling fluid; whereby a fully cured polyamide-epoxy resin coating is continuously and rapidly formed in-line on said strip of metal.

15. A process as in claim 14 wherein said fluid film of said solution is sprayed onto a side of said metal strip by applying hydraulic pressure to said solution to effect atomization of said solution onto the surface of said continuously moving strip of metal without admixing said solution in an atomized form with a propellant gas.

16. A process as in claim 15 wherein said strip is a galvinized steel strip.

17. A process as in claim 15 wherein said amine is n-butylamine.

18. A process as in claim 14, wherein said amine is a lower aliphatic amine.

19. A process as in claim 14, wherein said amine is n-hexylamine.

20. A process as in claim 14, wherein said amine is a cyclic amine.

21. A process of providing an elongated strip of metal with a thin continuous coating of an organic resin which comprises; continuously applying to at least one side of an elongated metal strip moving at a substantially constant speed a uniform fluid film of a solution of a polyamide resinous material containing terminal amino groups and an epoxy resinous material containing terminal epoxy groups in a halogenated hydrocarbon solvent containing at least about 50% by weight methylene chloride, said resinous materials being present in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight polyamide resinous material, and said solution containing as a buffering agent a basic organic amine having a boiling point of at least 250° F. and which is present in an amount which maintains the pH of said solution at about pH 9 to 9.5, exposing said fluid film on said strip to a temperature between about 1500° F. and 1700° F. for a period about 3 to 5 seconds to effect substantially immediate and complete curing of said film, and rapidly cooling said film and said strip to about room temperature by contacting with a cooling fluid; whereby a fully cured polyamide-epoxy resin coating is continuously and rapidly formed on said strip of metal.

22. An article comprising a structure having thereon a protective resin film coating which comprises a high-temperature reaction product of a polyamide resinous material containing terminal amine groups and an epoxy resinous material containing terminal epoxy groups in a

proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material reacted in situ at a temperature of between about 1000° F. and 2000° F. in the presence of high-temperature decomposition products of methylene chloride.

23. A metal strip having on at least one surface thereof a firmly adherent protective resin film coating which comprises a high-temperature reaction product of a polyamide resinous material containing terminal amine groups and an epoxy resinous material containing terminal epoxy groups in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material reacted in situ at a temperature between about 1000° F. and 2000° F. in the presence of high-temperature decomposition products of methylene chloride.

24. A protective resin film for a metal surface which comprises; a cured film of a high-temperature catalytic reaction product of a polyamide resinous material containing terminal amine groups and an epoxy resinous material containing terminal epoxy groups in a proportion of about 1 to 4 parts by weight epoxy resinous material for every one part by weight of polyamide resinous material, said catalytic reaction product being formed in situ at a temperature between about 1000° F. and 2000° F. in the presence of high temperature decomposition products of methylene chloride.

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RICHARD D. NEVIUS, *Primary Examiner.*

WILLIAM D. MARTIN, *Examiner.*

R. S. KENDALL, *Assistant Examiner.*