

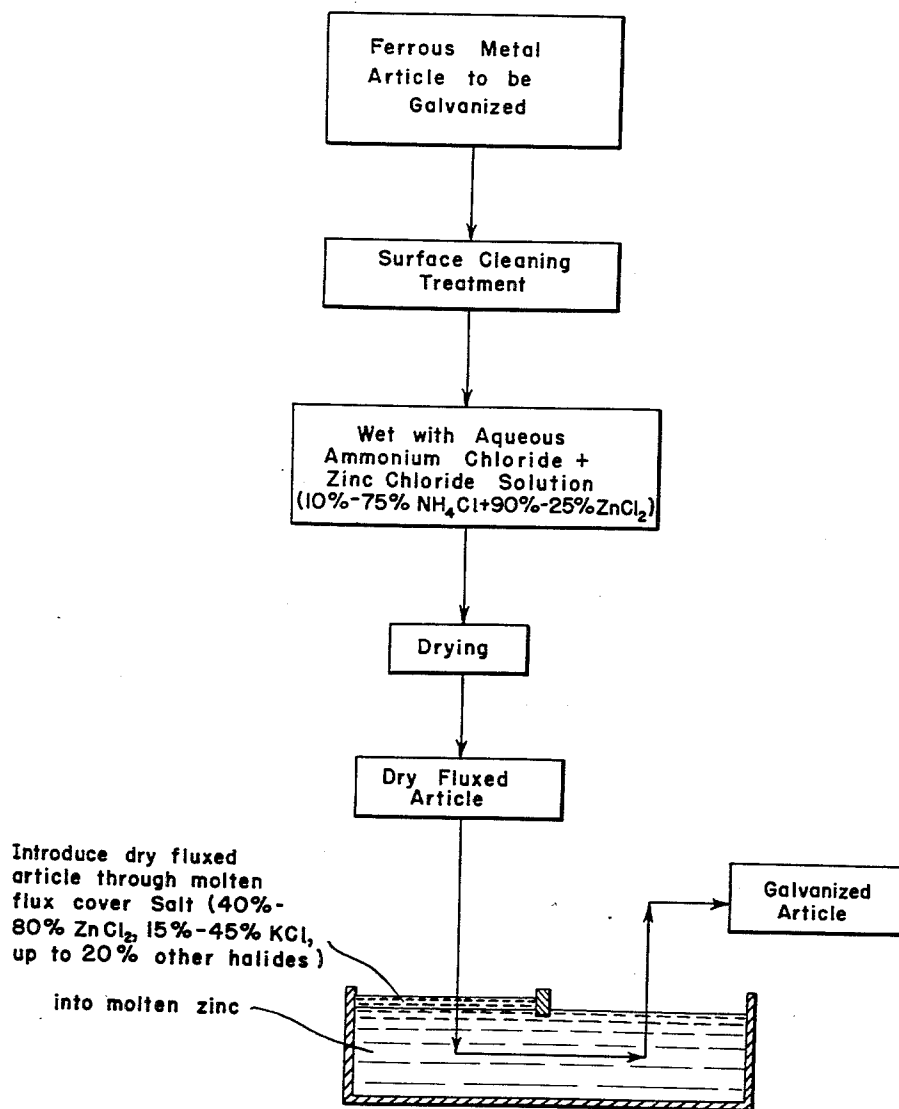
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METHOD OF HOT DIP GALVANIZING A FERROUS METAL

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METHOD OF HOT DIP GALVANIZING A FERROUS METAL

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This invention relates to galvanizing ferrous metal articles by the hot dip method, and is particularly directed to the provision of an improved procedure for fluxing the ferrous metal to insure formation thereon of a continuous, tightly adherent film of zinc. The process of the invention involves wetting the ferrous metal with an aqueous solution of a flux of ammoniacal zinc chloride and drying the solution to form a thin deposit of the flux on the article, after which the article is dipped in a molten bath of zinc covered by a fluid salt blanket which is at all times essentially free of ammonia (including ammonium salts).

Hot dip galvanizing of iron and steel to protect the ferrous metal from corrosion has been practiced on a large scale for more than a century. The procedure has always entailed fluxing the ferrous metal with a salt or salt mixture to clean it of oxides and other surface contaminants, so that the zinc may wet it effectively, and then immersing the fluxed article in a bath of molten zinc. The flux that has been most extensively used, and probably for the longest time, is zinc ammonium chloride. Traditionally, in hot dip galvanizing operations, the zinc bath has been maintained molten in a heated steel pot and has been covered with a fused layer of a molten salt flux consisting solely, or composed in large part, of zinc and ammonium chlorides (or zinc ammonium chloride). The long continued use of this flux is owing to its extensively effective cleaning action on the ferrous metal surface, which makes for easy formation of a continuous, adherent film of zinc, substantially free of pin holes and other imperfections.

Despite this prime virtue, however, the use of an ammoniacal flux in hot dip galvanizing is not without its serious disadvantages. The very effectiveness of the salt as a flux is owing to its rapid attack on the ferrous metal surface. This attack unfortunately does not stop with preparation of the metal surfaces for receiving the zinc coating—it promotes the formation of zinc-iron alloy interfacial layers of undesirably great thickness if the time of the galvanizing operation is not carefully controlled. Furthermore, a molten flux blanket composed to a substantial extent of ammonium chloride floating on the zinc bath undergoes a significant change in composition with continued use. It loses ammonia, in part by volatilization of the ammonium chloride itself and in part by volatilization of reaction products formed by its attack on the ferrous metal or on constituents (such as aluminum) of the zinc bath; and it accumulates iron. Such composition changes always lead to decreased fluidity of the flux and decreased effectiveness in its fluxing properties. It is periodically necessary to skim off the old flux blanket and replace it with a fresh melt of the flux salts. Changing the flux blanket necessitates discontinuing for the time being the galvanizing operation. Interruptions of this sort have become increasingly objectionable with increasing mechanization of the handling of the ferrous articles through the galvanizing operation.

Because of these disadvantages, considerable effort has been devoted to finding a fluxing procedure which will assure close control over the chemical attack of the flux

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on the metal surface, and will at the same time minimize the costly and time consuming skimming of old flux and replacement of it with new on the surface of the zinc bath. The only substantial advance heretofore made toward achieving these objectives has been the development of the so-called dry galvanizing process. This process involves immersing the ferrous article in an aqueous solution of ammoniacal zinc chloride, and drying the article to leave a thin deposit of the flux on the surface of the metal. The article is immersed in the molten zinc after it has been dried (whence the name "dry galvanizing," to distinguish this process from one in which the article is wetted with molten flux before being immersed in the molten zinc, a procedure called "wet galvanizing"). No flux, in the conventional sense, is employed on the surface of the zinc bath in dry galvanizing, for the residue of the salt film on the surface of the article as it is immersed in the zinc is relied on to activate the ferrous metal surface for reception of the zinc. There is, however, an accumulation of "ashes" or spent flux or both which accrues on the surface of the molten metal and which must be periodically skimmed off. Hence dry galvanizing, while it reduces substantially the adverse effects of uncontrolled fluxing of the ferrous metal surfaces and excessive loss of aluminum from the zinc bath, does not avoid the need for periodic skimming, and it increases the difficulty of maintaining a good clean and fluid surface on the zinc bath.

The present invention provides an improved galvanizing process which combines the best features of dry and wet galvanizing while eliminating largely the disadvantages of both. The process of the invention entails fluxing the ferrous metal article substantially by the procedure of dry galvanizing, using zinc ammonium chloride as the active flux salt, and maintaining a fluid protective blanket of an ammonia-free salt mixture on the bath of molten zinc. The salt blanket provides a thinly fluid protective cover on the molten zinc; and in accordance with the invention it is substantially free of ammonia (or any ammonium salt) and has the property of remaining free of ammonia by favoring volatilization of such ammonia as is introduced into it by the flux-coated ferrous metal articles. Thus the salt blanket is of stable composition which retains its fluidity for prolonged periods of time, and need only be replenished from time to time by fresh additions of the same composition to make up for drag-out or other losses. By use of the process of the invention, interruption of the galvanizing operation to skim the surface of the molten zinc is eliminated.

The new galvanizing method comprises wetting the ferrous metal article with an aqueous ammoniacal zinc chlorides solution, then drying the article (either at room temperature or by heating to a temperature which may range up to 400° F. or more) and then introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon. The salt blanket is composed predominantly of zinc chloride (constituting 40% to 80% by weight of the blanket) and potassium chloride (constituting 15% to 45% by weight of the blanket), and it preferably in addition contains other halides (especially chlorides) in amounts up to 20% by weight; its melting point should be well below 700° F., and it should be thinly fluid at that temperature. The salt blanket as prepared is substantially free of ammonia (and ammonium salts), and remains substantially free thereof during use. Ammonia compounds introduced into the salt blanket by introduction of the flux-coated ferrous metal articles rapidly are dissipated by volatilization, so that even after a prolonged period of use the blanket contains only a very small quantity of ammonia (generally not over a 1% or 2%). It is therefore a highly stable composition which retains its high degree of fluidity and protective

quality indefinitely. It is only necessary to add make-up amounts of the same salt composition from time to time, without having to skim the bath at any time.

The new galvanizing method may be carried out either as an intermittent operation in which the articles to be galvanized are handled more or less manually, or as a continuous operation in which the handling of the articles through the several steps is largely or even completely mechanized. It is one of the advantages of the invention, however, that it permits mechanized handling of the articles through the galvanizing bath without need to interrupt operations at intervals to skim spent flux or ashes from the bath. Articles such as iron and sheet metal are most easily passed through the galvanizing operation in an essentially continuous operation; but discrete articles such as pails, cans, tanks, and other hardware items are most conveniently handled on a batch basis, especially if their number is not large and does not justify installation of a suitable conveyor system.

The accompanying flow sheet schematically shows the sequence of steps employed in carrying out a preferred embodiment of the invention, which embodiment is described below in considerable detail.

The articles to be galvanized are first thoroughly cleaned. The invention contemplates the same sort of cleaning that now is practiced in conventional galvanizing operations. It involves usually a thorough degreasing in either or both a liquid or vapor degreasing chamber and an alkaline cleaning solution, and then a pickling operation in acid.

As soon as practical after cleaning, the article is wetted with the ammoniacal zinc chloride flux solution. This operation can be carried out in any convenient way. For example, the articles may be dipped in a bath of the flux solution, or the flux solution may be applied by spraying it on the articles. The flux solution itself is primarily an aqueous solution of zinc and ammonium chlorides. These salts are preferably used in the proportions of 10% to 75% ammonium chloride by weight of the mixture of salts and 90% to 25% zinc chloride by weight of the mixture. Preferably these salts are dissolved in water to a concentration of from 1/2 to 3 pounds of the mixture per gallon.

Instead of using a mixture of zinc and ammonium chloride ($\text{ZnCl}_2 + \text{NH}_4\text{Cl}$) equally satisfactory results may be obtained using a zinc ammonium chloride (e.g. $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ or $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$) as the active salt dissolved in the aqueous flux solution.

In addition to the zinc and ammonium chlorides, or zinc ammonium chloride, the flux solution advantageously also contains an organic frothing agent such as glycerine, a soluble glucoside or carbohydrate, tallow emulsion, or the like. The frothing agent facilitates the fluxing action of the zinc ammonium chloride. Any of the frothing agents used in galvanizing fluxes may be employed in carrying out the present invention. The amount of frothing agent employed ordinarily is from 0.1% to 1% by weight of the solution. Also a wetting agent may with advantage be present in the flux solution, to insure that it effectively wets all parts of the article to be galvanized. Any conventional wetting agent may be employed for such purpose.

By way of example, an aqueous solution containing 2 pounds per gallon (240 grams per liter) of a mixture composed of 40% by weight of ammonium chloride and 60% by weight of zinc chloride, about 1 1/2 ounces per gallon (11 grams per liter) of glycerine, and about 1/4 ounce per gallon (2 grams per liter) of a wetting agent such as sorbitan monopalmitate, is a very satisfactory flux solution.

Most commonly the flux solution is applied hot to the article to be galvanized. In general it is heated to a temperature above 120° F., up to say, 190° F. It is desirable to retain the articles immersed in (or otherwise in contact with) the hot flux solution until the articles have

become heated substantially to the temperature of the solution. Then when the article is withdrawn from the solution it dries rapidly by evaporation of the water from the adhering film of flux solution. Rapid drying is desirable, but drying should be conducted under conditions which do not cause injury to the flux film. Drying ordinarily is effected by simply exposing the articles, after withdrawal from the flux solution, to the atmosphere. Drying may, however, be effected in a drying oven in which the articles are heated to a temperature up to 400° F. or higher. The time required for drying, while short, varies with the temperature. Drying should be allowed to continue long enough for the article to be quite completely dried, but there is no advantage for it to continue longer and it may even have the disadvantage of promoting undesirable attacks of the flux on the ferrous metal. The dried article has on its surface a thin film made up of a residue of the zinc and ammonium chlorides and of such reaction products as have formed in consequence of the attack of the flux on the surface of the metal.

The dried article should be immersed in the molten zinc galvanizing bath as promptly as is practical after drying. It is desirable to minimize exposure of the article to the air after drying and before dipping in the molten zinc bath to conserve the heat of the dried article and to minimize the opportunity for atmospheric oxidation or other attack on its flux-coated surface. Immersion involves passing the article through the molten salt blanket covering the molten zinc to beneath the zinc surface and then withdrawing the article again from the zinc bath. The surface of the merging article is coated with a thin, adherent film of zinc. The article is cooled to room temperature in any desired manner, advantageously by quenching with water.

In accordance with the invention, the molten salt blanket floated on the molten zinc is initially prepared free from ammonia and ammonium salts, and in fact has the property of favoring elimination of ammonia by volatilization. This salt blanket is composed predominantly of 40% to 80% by weight of zinc chloride and 15% to 45% by weight of potassium chloride. Advantageously it also contains up to 20% by weight of other halides, particularly chlorides of the alkali and alkali earth metals. Very satisfactory salt blankets are composed of 50% to 75% by weight of zinc chloride, 15% to 45% by weight of potassium chloride, and up to 20% by weight of other halides, e.g. 5% to 15% by weight of sodium chloride and up to 10% by weight of an alkali earth metal chloride such as calcium chloride or magnesium chloride. Within this composition range, especially satisfactory results have been attained with salt mixtures composed of 55% to 65% by weight of zinc chloride, 15% to 35% by weight of potassium chloride, 8% to 12% by weight of sodium chloride, and 3% to 7% by weight of calcium chloride.

Zinc chloride is the main ingredient of the salt blanket, and is combined with potassium chloride in proportions such as to yield a mixture which is completely molten and thinly fluid at a temperature well below 700° F. Potassium chloride is employed both because in combination with zinc chloride it yields a low melting mixture of low viscosity, and because its presence in the mixture favors elimination of such ammonia as becomes introduced into it. The addition of other halides is desirable both to economize on the zinc and potassium chlorides and to improve fluidity and stability of the fused mixture. Sodium chloride is advantageous because it is an inexpensive diluent for the salt mixture and because in proper quantities it improves stability of the mixture. A small amount of calcium chloride is desirable for similar reasons, and also to help lower the melting point and the viscosity when molten of the mixture to which sodium chloride has been added. Other salts which may be used in some cases with advantage in the

mixture, either in addition to or as substitutes for the calcium chloride and for a part or all of the sodium chloride, include magnesium chloride, sodium aluminum fluoride, tin chloride, barium chloride, and strontium chloride.

The salt mixture should be thinly fluid at the temperature of the zinc bath on which it floats as a covering blanket, and it should have a low, watery viscosity at such temperature so as to flow readily over the entire surface of the zinc bath and to drain quickly and quite completely from the ferrous metal articles withdrawn from the molten zinc. To this end the flux blanket preferably is composed of salts in such proportions as to yield a mixture which is completely molten at 650° F., and preferably at 600° F. or lower. It is possible, with salt mixtures of the character contemplated, to attain melting points (temperature at which the mixture is completely molten) below 500° F.

In addition to low melting point and low viscosity, the salt mixture should possess a high degree of stability at the galvanizing temperature. It should not exert a corrosive or other undesirable attack on either the ferrous metal articles being galvanized, or on the molten zinc or any component of the zinc bath. It should not tend to change in composition during use to the extent that it increases substantially in melting point or viscosity. Hence it should neither tend to accumulate substantial amounts of foreign salts or other compounds from the zinc or ferrous metal, and should not tend to decompose or lose any of its ingredients preferentially.

An example of a particularly satisfactory salt mixture which melts at a temperature below 500° F. and possesses in a high degree the above mentioned properties of low viscosity and high stability at the galvanizing temperature, is one composed nominally of 60% by weight of zinc chloride, 25% by weight of potassium chloride, 10% by weight of sodium chloride, and 5% by weight of calcium chloride.

The salt mixture may be deposited in solid form on the surface of the molten zinc, where it is melted by the heat of the zinc. The zinc bath is heated to about 825° F. or 850° F. (a normal galvanizing temperature), during galvanizing and the salt mixture is fused and heated to such temperature by the heat of the molten metal. The fused salt, being of low viscosity, spreads uniformly over the entire surface of the molten metal. Preferably enough is employed to cover the surface of the zinc with a layer about one-half inch, more or less, in thickness.

When the dry fluxed ferrous metal is introduced through the fused salt blanket into the molten zinc, the residue of ammoniacal compound on the ferrous surface fuses and mixes with the salt blanket. However, it is quite rapidly expelled again, by volatilization, at the temperature at which the salt blanket is maintained during galvanizing. Consequently it does not cause any significant change to occur in the composition of the salt blanket. In particular it does not accumulate therein in sufficient quantity to cause the blanket to react undesirably with the molten zinc or any other component (such as aluminum) of the galvanizing bath, or to cause it to attack the ferrous metal or promote an excessive thickness of iron-zinc alloy at the interface of the ferrous metal and the zinc coating. The particular salt blanket composition mentioned above by way of example will not generally accumulate more than about 0.25% by weight of ammonia even after prolonged use in a galvanizing operation according to this invention.

Some iron does enter the fused salt blanket, by reason of fusion therein of ferrous reaction products of the ammoniacal flux with the ferrous metal article. It is quickly reduced by reaction with the molten zinc, however, and collects in the dross which forms during operation of the process.

The ferrous metal is held immersed in the molten zinc

only long enough to be wetted by it, and is then withdrawn again from the zinc bath. It is preferable practice to withdraw the articles from the bath at a point when the bath is free of molten salt, in order to avoid

picking up salt on the emerging zinc-coated article. To this end a partition may extend across the surface of the zinc bath, to confine the molten salt blanket to that part of the bath when the articles being coated are introduced, and to exclude it from the surface of the bath in the vicinity where the articles are withdrawn. In some cases such partition may be omitted, and the surface of the zinc bath may be kept free of molten salt in the region where the articles emerge by skimming. In other cases special forms of galvanizing pots may be provided to permit withdrawal of the articles without bringing them in contact with the molten salt blanket. In yet other cases, especially where the molten flux has a low melting temperature and a low viscosity, it may be satisfactory to withdraw the articles through the salt blanket, and to wash off any thin film of salt adhering to them.

It is desirable to cool the articles promptly after they emerge from the zinc bath, to prevent undue growth of the iron-zinc alloy at the interface of the zinc coating and the basic metal. Cooling advantageously is by a water quench, either in a pool of water or by a water spray. It is undesirable to hold the articles in the quench water longer than is necessary to cool it to a temperatures low enough to substantially stop further development of the interfacial alloy. The quenched articles should still be hot enough to dry rapidly by evaporation of the water adhering to its surface. Often for this reason, it is preferred to use hot water (at a temperature from 120° F. to 200° F.) for quenching.

If the galvanized article has been withdrawn from the molten zinc bath through the fused salt blanket, salt adhering to it may be washed off by the quench water. Salt removed from the bath cover in this manner (so-called "drag-out") cannot conveniently be recovered. It is replaced from time to time by simply adding make-up amounts of the original salt mixture to the surface of the zinc bath.

The zinc coating on properly cleaned articles galvanized by the method of this invention is of excellent quality. It is of uniform thickness, tightly adherent to the underlying metal, substantially free of pin holes, and with a desirably thin layer of iron-zinc alloy at the interface between the ferrous metal and the zinc coating. Control of the attack of the ammoniacal flux on the ferrous metal is readily achieved by controlling the concentration and relative proportions of zinc and ammonium chlorides in the flux solution, and by controlling the temperature and duration of the drying operation. The process is admirably adapted to being highly mechanized, for the step of coating with flux solution, drying, and carrying through the galvanizing bath can all be performed as the articles being galvanized are being conveyed on a mechanical conveyor system. The stability and low viscosity of the fused salt blanket which covers the molten zinc bath eliminates the need for periodic skimming of the bath. Owing to some or all of these desirable features, the new process may be used with advantage in almost all galvanizing operations.

I claim:

1. The method of galvanizing a ferrous metal article which comprises wetting the article with an aqueous ammoniacal zinc chloride solution, drying the article, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket being composed predominantly of 40% to 80% by weight of zinc chloride and 15% to 45% by weight of potassium chloride, said salt blanket having a melting point below 700° F. and being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

2. The method of galvanizing a ferrous metal article

which comprises wetting the article with an aqueous solution of a flux mixture of zinc and ammonium chloride containing from 10% to 75% by weight of ammonium chloride, drying the article to leave a thin residue of flux thereon, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket consisting essentially of 50% to 75% by weight of zinc chloride, 15% to 45% by weight of potassium chloride, and up to 20% by weight of other halides of the alkali and alkali earth metals, said salt blanket having a melting point below 650° F. and being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

3. The method of galvanizing a ferrous metal article which comprises wetting the article with an aqueous ammoniacal zinc chloride solution, drying the article, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket consisting essentially of 55% to 65% by weight of zinc chloride, 15% to 35% by weight of potassium chloride, 5% to 15% by weight of sodium chloride, and up to 10% by weight of an alkali earth metal chloride, said salt blanket having a melting point below 600° F. and being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

4. The method of galvanizing a ferrous metal article which comprises wetting the article with an aqueous solution of a flux mixture of zinc and ammonium chlorides containing from 10% to 75% by weight of ammonium chloride, drying the article to leave a thin residue of flux thereon, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket containing approximately 60% by weight of zinc chloride, approximately 25% by weight of potassium chloride, approximately 10% by weight of sodium chloride, and approximately 5% by weight of calcium chloride and having a melting point below 500° F., said salt blanket being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

5. The method of galvanizing a ferrous metal article which comprises immersing the article in an aqueous solution containing from ½ to 3 pounds per gallon of a mixture comprising from 10% to 75% by weight of ammonium chloride and the balance essentially all zinc

chloride, drying the article, introducing the dried article into a bath of molten zinc, through a molten salt blanket floating thereon, said salt blanket being composed predominantly of zinc and potassium chlorides and having a melting point below 650° F., said salt being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

6. The method of galvanizing a ferrous metal article which comprises cleaning the article, immersing the cleaned article in an aqueous ammoniacal zinc chloride solution, heated to a temperature above 120° F. until the article is heated substantially to the temperature of the solution, withdrawing the article from the solution and drying it substantially completely, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket being composed predominantly of 40% to 80% by weight of zinc chloride and 15% to 45% by weight of potassium chloride, said salt blanket having a melting point below 700° F. and being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

7. The method of galvanizing a ferrous metal article which comprises immersing the article in an aqueous solution of a flux mixture of zinc and ammonium chlorides containing from 10% to 75% by weight of ammonium chloride heated to a temperature above 120° F. until the article is heated substantially to the temperature of the solution, withdrawing the article from the solution and allowing it to become substantially completely dried, introducing the dried article into a bath of molten zinc through a molten salt blanket floating thereon, said salt blanket consisting essentially of 50% to 75% by weight of zinc chloride, 15% to 45% by weight of potassium chloride, and up to 20% by weight of other halides of the alkali and alkali earth metals, said salt blanket having a melting point below 650° F. and being and remaining substantially free of ammonia, and withdrawing the article with a thin adherent coating of zinc from the zinc bath.

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