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UTILIZING GALVANIZER'S WASTE

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This invention relates to utilizing galvanizers' waste; and it comprises a method wherein galvanizers' skimmings in coarsely broken form are leached to obtain a strong liquor and a residue
5 nearly free of ammonia and suitable for making zinc chlorid, the liquor containing $ZnCl_2$ and NH_4Cl in approximately 1:1 ratio being then treated to obtain a crystalline, fusible double salt, either with a 1:2 or a 1:3 ratio, as the case may
10 be, suitable for return to the galvanizers, the additional NH_4Cl usually necessary being obtained by an addition of that salt or by a subtraction of $ZnCl_2$; in the latter event, with the production of an ammoniated zinc chlorid, $ZnCl_2 \cdot 2NH_3$, also
15 useful as a flux; and it further comprises certain new and useful flux mixtures, one being a physical mixture of said ammoniated zinc chlorid with the 1:2 or 1:3 double salt; all as more fully hereinafter set forth and as claimed.

In galvanizing, clean pickled iron or steel is dipped into or passed through a body of molten zinc and withdrawn, carrying a film coating of zinc. In this operation it is necessary that the
20 two metals come into contact with clean, truly metallic surfaces and the zinc is kept covered with a molten floating cover, to prevent access of air and maintain a bright surface, free of oxide. Often the pickled iron is passed through or dipped
25 in a solution of fluxing salts prior to contact. The floating cover or flux layer sometimes contains organic matter, such as glycerin, to give viscosity and a frothy character; this being most desirable at the point where the iron enters the bath as it serves to remove moisture without per-
30 mitting spattering of molten zinc. The body of the flux is a molten saline composition and should be thin and free flowing. It is usually prepared from sal-ammoniac; ammonium chlorid. The composition of this salt layer is constantly chang-
35 ing and its fusibility lessening; and when it becomes comparatively infusible, some of it is skimmed off and discarded and the layer replenished; ordinarily by addition of sal-ammoniac in
40 some way. These skimmings are a galvanizer's waste. They are of complex and varying composition but since they contain ammonia in some form of combination and also chlorids, they may
45 be regarded as containing sal-ammoniac. These skimmings will be hereinafter called "sal-ammoniac skimmings". In the art they are sometimes called "sal skimmings".

In the present invention, the waste is treated in certain methodical ways to recover fusible
50 saline materials which can go back for use on the

galvanizers' bath or can be used for other purposes.

As stated, the composition of the floating saline layer or "flux" is constantly changing, but it al-
ways contains zinc chlorid, ammonium chlorid
5 and ammonia. Many complex combinations of zinc chlorid with ammonium chlorid and with ammonia are known; and some, or all, of them occur in the floating saline layer at one time or
10 another.

Several functions are required of the flux layer. One is that of excluding air, thereby preventing or diminishing formation of zinc oxid. For this
purpose it should be free flowing and of low vis-
cosity. Another is that of dissolving zinc oxid,
15 if it is formed; it should be a free solvent of zinc oxid but should attack zinc as little as may be. The various flux compositions mentioned vary among each other in these respects. And there
are really two questions involved: one being main-
20 tenance of the floating layer of the best composition as a compromise of these requirements and the other is that of a composition for replenishment of the floating layer as it loses fusibility by
taking up zinc oxid and losing volatiles.

As stated, replenishment in practice is nearly
25 always by sal-ammoniac; this being sometimes by direct addition of the solid commercial salt to the molten bath. Ammonium chlorid alone, that is not occurring as such a double salt as it forms
30 with zinc chlorid, vaporizes without melting at the temperature of molten zinc, $419^\circ C.$, and the practice is therefore wasteful, losses by volatilization being large. Sometimes a physical mixture
35 of powdered skimmings and sal-ammoniac is used; and this practice is also wasteful for the same reason. These skimmings in any event are not of the right composition, containing too much
infusible matter and being basic enough to dis-
place NH_3 as such; as a gas.

In the present invention, various compositions
40 are made by methodical utilization of skimmings; these compositions being suitable for direct use as a flux cover for molten zinc and for replenishment of the cover. Their use obviates much of
45 the waste due to the present method of replenishing the flux cover with sal-ammoniac; and gives better protection; it enables better regulation of the composition of the cover and a nearer ap-
50 proach to maintenance of ideal conditions therein.

Galvanizers' waste is usually in the form of
hard crusts or chunks. I have found that by
coarse grinding, this material can be efficiently
55 leached with water to give a concentrated saline

solution. On contact with the water, the lumps heat up and swell without disintegrating, and the penetration of the leaching water is good. The leached residual solid material is an economical material for the production of commercial zinc chlorid for wood saturating and other purposes. It is a porous, readily soluble form and contains negligibly small amounts of ammonia. It contains chlorin in an amount equivalent to about 20 per cent of that required in forming zinc chlorid, thereby reducing the amount of HCl necessary. The leached material is a better and more economical source of zinc chlorid than the original skimmings.

The leach liquors contain zinc chlorid and ammonium chlorid. These occur in varying proportions, often in about equimolecular proportions; in a 1:1 ratio. The liquid is somewhat basic, which may be attributed to the presence of zinc oxid in excess or of ammonia in excess. The leach liquors can be directly evaporated to dryness and fusion, producing a fused mixture of zinc chlorid and ammonium chlorid. This can be run into water-tight cans and allowed to solidify, directly producing a flux which can be returned to the galvanizer. Because of the hygroscopic qualities of the material thus made, however, and for other reasons, it is not as satisfactory as various preparations made as hereinafter specified. It carries not more than one NH_4Cl for each ZnCl_2 ; and this is too little for satisfactory results. In using it, the galvanizer must ordinarily add sal-ammoniac also as a physical admixture; and this is unsatisfactory for the reasons stated.

In the present invention the leachings are treated in various ways to obtain crystalline compounds better adapted for the galvanizer's use than either the concentrated and solidified liquor just described or sal-ammoniac itself.

Zinc chlorid combines with various proportions of NH_3 to form what may be called ammoniated chlorids. A crystalline composition readily produced from the leachings is the di-ammoniated chlorid, $\text{ZnCl}_2 \cdot 2\text{NH}_3$. This is fusible, freely mobile and forms an excellent cover. It has, however, but little solvent power for zinc oxid. At the temperature of the molten zinc bath it loses NH_3 and becomes the mono-ammoniated compound, $\text{ZnCl}_2 \cdot \text{NH}_3$. This latter, insofar as covering is concerned, is ideal because of its high mobility. It is more stable toward decomposition by heat than any of the other compositions hereinafter described. Because of its mobility and low viscosity, at the point where the entering metal passes through the flux there is not even momentary exposure of molten zinc to the atmosphere. In respect to covering power, it is decidedly better than any of the other fluxes. The mono-ammoniated zinc chlorid is however not of a physical character permitting convenient storage, shipment and use. But, as stated, the di-ammoniate is converted into the mono-ammoniate in use.

There are several double compounds of zinc chlorid and ammonium chlorid. Two that can be conveniently prepared from the leach liquors are $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ and $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ which may be conveniently referred to as the 1:2 and the 1:3 double salts.

Both of these double salts on the galvanizers' bath are fusible and form fair coverings and both have a solvent power for zinc oxid. Both are good agents for replenishing an existing cover and both may be regarded as convenient means for

introducing sal-ammoniac. Naturally the 1:3 salt is better for this purpose than the 1:2.

As stated, I have found that the galvanizers' waste can be leached with water to produce a solution containing zinc chlorid and ammonium chlorid in a molecular ratio approximating 1:1. I have found that by evaporating the leachings by heat and continuing the heating and concentration until the liquid is at a temperature of about 130°C ., on cooling there is a copious deposition of crystals of the 1:2 compound. About 50 per cent of the ammonium chlorid present comes out as this salt, leaving a mother liquor correspondingly impoverished in ammonium chlorid and relatively richer in zinc chlorid. By taking another portion of leachings and adding ammonium chlorid to obtain a 1:2 ratio and heating and concentrating to a final temperature of about 119°C ., on cooling a crop of crystals is obtained of another and different composition, the product now being a double salt with a 1:3 ratio. As before, a mother liquid is left poor in ammonium chlorid. Both these salts, the 1:2 and the 1:3, are desirable fluxes for the galvanizer's use; both serve well for replenishment; both are recovered in a physical form which enables easy separation; and both are convenient for packaging and storing, because of their non-hygroscopic and permanent properties. The 1:2 salt however is not quite as non-hygroscopic as the 1:3. I regard the 1:3 salt as the most convenient and economical form in which the galvanizer can add replenishing sal-ammoniac.

In making the 1:2 salt without addition of ammonium chlorid to the leachings, the residual liquor is, as stated, rich in zinc chlorid and it may be marketed in concentrated form as a tinning or soldering flux. The same is true where the liquor has been enriched with ammonium chlorid, either by more salt added as such or by additions of ammonia and HCl and then the double salt formed and removed. Sometimes, after the separation of the crop of crystals in the way described, it is economically worth while to add ammonium chlorid to the mother liquor rich in zinc chlorid and repeat the operation, obtaining the 1:2 or the 1:3 salt, as the case may be.

It is possible, and often economically worth while, to unite the processes previously described, first, adding ammonia to leaching liquors to produce ammoniated zinc chlorid and a mother liquor relatively rich in ammonium chlorid; and then treating this mother liquor to produce the 1:2 or the 1:3 double salt. Or, the mother liquor from a production of ammoniated zinc chlorid may be used as a source of ammonium chlorid for production of double chlorids from another portion of leachings; either in the 1:2 or the 1:3 ratio. As will appear hereinafter, there is commercial utility in certain physical mixtures of an ammoniated zinc chlorid and a double chlorid, so that it is frequently worth while to treat one portion of liquor in the one way and another portion in the other way.

Comparing the described bodies among each other, the best covering flux is a mono-ammoniated zinc chlorid; best because of its low viscosity and low melting point. It is, however, inconvenient to package and store. The di-ammoniated has all the virtues of the mono-ammoniated and is, further, easy to make, package and ship. The best of the fluxes for reacting with zinc oxid is the 1:3 double salt but it is relatively viscous in molten form. The 1:2 double salt in its physical properties is about the same but it

has less reactive power with zinc oxid; it imports less sal-ammoniac into the bath.

In use the covering layer loses ammonium chlorid and ammonia as vapor and it steadily tends toward a composition representing zinc chlorid with a little ammonia. It is usually discarded before all the ammonium chlorid disappears.

I regard di-ammoniated zinc chlorid as being the best covering addition, all things considered, but I regard the 1:3 double salt as the best medium for replenishment of ammonium chlorid. With di-ammoniated zinc chlorid and the 1:2 and the 1:3 salts at hand the galvanizer is in a position to control, quite accurately, the composition of his working flux; using each of these individually as the circumstances may warrant. But for general purposes it is better to supply him regulated physical mixtures of ammoniated zinc chlorid and of double salts. Physical mixtures of this kind are easy to make, package and use. They are permanent in air. The particular mixture depends somewhat on the galvanizer's needs. When working at temperatures above 430° C. a mixture of di-ammoniate and the 1:2 salt in about equimolecular proportions is good. As a matter of theory, a mixture of mono-ammoniated zinc chlorid with a composition containing one molecule of zinc chlorid and one of ammonium chlorid should be best; and this can be made by mixing mono-ammoniate with leachings evaporated to dryness; but the mixture is too hygroscopic for convenience in shipping and handling. This mixture, however, combines low viscosity, minimum loss by volatility and maximum solvent powder for zinc oxid in a desirable way.

A physical mixture of granular, crystalline di-ammoniate with either the 1:2 or the 1:3 double salt, also in granular crystals, is a highly desirable article. Provision of such an article also gives the maximum utilization of the zinc chlorid and ammonium chlorid in the leachings. Addition to the galvanizing bath of a mixture of the ter has been evaporated and 22 pounds of the 1:3 double salt in equimolecular proportion with respect to zinc chlorid is equivalent in effect to replenishment in the fluxing bath of mono-ammoniated zinc chlorid and ammonium chlorid.

In a specific embodiment of the present invention making the di-ammoniated zinc chlorid, certain leachings carrying 37 per cent zinc chlorid and 12 per cent ammonium chlorid were alkalinized with ammonia. The amount of ammonia required as gaseous NH_3 was 6.25 per cent by weight of the leachings. In using gaseous NH_3 it was necessary to add water; the amount being 1.5 times the weight of gas. Instead of using ammonia in gaseous form, the commercial 25 per cent solution can be added. The alkalinized liquid was heated to 90° C. The liquid was cooled to room temperature (about 20° C.), and deposited a crop of crystals of di-ammoniated zinc chlorid, the amount being 31 pounds per 100 pounds of the original leachings. The mother liquor was drained off and concentrated, finishing at about 119° C. On cooling, a crop of crystals of 1:3 double salt was deposited, the amount being approximately 7 pounds per 100 pounds of the original leach liquor. The mother liquor was reconcentrated to 119° and a second crop of crystals of 1:3 double salt was deposited. This procedure could be repeated until all of the water has been evaporated and 22 pounds of the 1:3 salt obtained, but in practice the volume of the mother liquors was maintained at the desired

point by combining the mother liquors of several crystallizations.

In the preceding example the products were diammoniated zinc chlorid and 1:3 double salt. In another embodiment 4.5 pounds of NH_3 were added to 100 pounds of leachings and 26 pounds of $\text{ZnCl}_2 \cdot 2\text{NH}_3$ obtained, then about 7 pounds of the 1:3 double salt as before. Then by concentrating the mother liquor to 130° C. and cooling, a crop of crystals of the 1:2 salt was deposited, the amount being 10 pounds per 100 pounds of leachings. The mother liquor was concentrated to 130° and more crystals of the 1:2 salt recovered as above. This procedure was repeated until about 20 pounds of the 1:2 crystals had been obtained. The final mother liquor was returned to another portion of leachings. It was possible to send the mother liquor to market after the ordinary purification and concentration as a tinning and soldering flux; but this was not done in this instance.

Where it is desired to make only the 1:2 salt, the leachings may be concentrated directly to a finishing temperature of 130° C. Upon cooling, crystals of the 1:2 salt are obtained, but no 1:3 salt.

A particularly desirable and marketable composition is a physical mixture of one part by weight of the diammoniated zinc chlorid and four parts by weight of the 1:3 double salt, both in dry, coarse, crystalline condition. The mixture can be fused into a cake but it is more convenient to use it in powdered form.

It is possible to remove zinc chlorid in the ammoniated form from the leachings by alkalinization with ammonia and concentrate the mother liquor to recover ammonium chlorid. Where it is desirable to obtain a particularly pure zinc chlorid without too much evaporation of water, it is a desirable expedient to make di-ammoniated zinc chlorid, and then fuse this to obtain zinc chlorid and NH_3 which is recycled; being sent back to fresh leachings.

Similarly, mono-ammoniated zinc chlorid can be made from the di-ammoniated zinc chlorid produced as described by distilling off one-half the ammonia; the expelled ammonia being led back to a portion of leach liquor. Expulsion of ammonia is at about 400° C.

In one way of looking at the present invention it is furnishing the galvanizers with sal-ammoniac in a form in which it can be more economically employed; and in another, it is returning to the galvanizer discarded ammonium chlorid. Ammonium chlorid which may be added in the manufacture of fluxes in the way described is more economically utilized than where a flux is, so to speak, extemporized by a galvanizer in casting solid sal-ammoniac on the bath.

In the present invention, discarded skimmings from the galvanizers are treated to subtract zinc oxid and returned. The leaching process extracts salines from a residue consisting mainly of zinc oxid; and these salines are returned to the galvanizer.

What I claim is:—

1. In the utilization of galvanizers' sal-ammoniac skimmings by improved processes wherein the inert components of said skimmings are separated and removed from the active and desirable fluxing materials, the steps which comprise leaching said skimmings with water to make a strong leach liquor, adding ammonia to the liquor, heating somewhat, and cooling to produce a crop of diammoniated zinc chlorid.

2. In the utilization of galvanizers' sal-ammoniac skimmings by improved processes wherein the inert components of said skimmings are separated and removed from the active and desirable fluxing materials, the steps which comprise leaching said skimmings with water to make a strong leach liquor, adding ammonia to the liquor, heating somewhat, cooling to produce a crop of diammoniated zinc chlorid with separation of a mother liquor, concentrating the mother liquor and finishing at a high temperature, and cooling to produce a crystallization of a double salt of zinc chlorid and ammonium chlorid.

3. The process of claim 2 wherein the finishing is at a temperature of about 119° C.

4. The process of claim 2 wherein the finishing is at a temperature of about 130° C.

5. In the utilization of sal-ammoniac skimmings from a galvanizing bath by improved processes wherein the inert components of said skimmings are separated and removed from the active and desirable fluxing materials, the steps which comprise leaching the skimmings with water, adding ammonia to the leach liquor and separately crystallizing therefrom first diammoniated zinc chlorid and then a double chlorid of zinc and ammonium and returning said compounds to the galvanizing bath.

6. In the utilization of sal-ammoniac skimmings from galvanizing baths, the process which comprises separating zinc oxid from the saline matter contained in the skimmings and returning said saline matter to a galvanizing bath.

7. In the utilization of galvanizers' sal ammoniac skimmings, by improved processes wherein the inert components of said skimmings are separated and removed from the active and desirable fluxing materials, the steps which comprise leaching the skimmings with water to obtain a liquid containing zinc chlorid and ammonium chlorid, increasing the ratio of ammonium chlorid to zinc chlorid in the liquid and thereafter crystallizing out a double salt of zinc chlorid and ammonium chlorid.

8. In the process of claim 7, the method of increasing the ratio of ammonium chlorid to zinc chlorid which comprises subtracting zinc chlorid by adding ammonia and removing zinc chlorid as the di-ammoniate salt.

9. In the process of claim 7, the method of increasing the ratio of ammonium chlorid to zinc chlorid which comprises adding ammonium chlorid to said liquid.

10. In the utilization of galvanizers' sal-ammoniac skimmings, the process which comprises leaching said skimmings with water to separate the inert components from the active fluxing materials and crystallizing said active fluxing materials from the leachings in a form suitable for return to the galvanizing bath.

11. In the utilization of galvanizers' sal-ammoniac skimmings, the process which comprises leaching said skimmings with water to separate the inert components from the active fluxing materials, separately recovering diammoniated zinc chlorid and a double salt of zinc chlorid and ammonium chlorid from the leachings in the form of granular crystals and then mixing said diammoniated zinc chlorid and said double

salt, the mixture being suitable as a galvanizer's flux.

12. In the utilization of sal-ammoniac skimmings from galvanizers' flux a process of making from such skimmings a material useful in replenishing the flux which comprises leaching the skimmings with water so as to make a strong solution of zinc chlorid and ammonium chlorid, treating said solution with ammonia, crystallizing diammoniated zinc chlorid from the treated solution with separation of a mother liquor, crystallizing from the mother liquor a double salt of zinc and ammonium chlorid in a molecular ratio of 1:3 and mixing said double salt and said diammoniated zinc chlorid.

13. In the utilization of sal-ammoniac skimmings from galvanizers' flux a process of making from such skimmings a material useful in replenishing the flux which comprises leaching the skimmings with water so as to make a strong solution of zinc chlorid and ammonium chlorid, treating said solution with ammonia, crystallizing diammoniated zinc chlorid from the treated solution with separation of a mother liquor, crystallizing from the mother liquor a double salt of zinc and ammonium chlorid in a molecular ratio of 1:2 and mixing said double salt and said diammoniated zinc chlorid.

14. In the utilization of sal-ammoniac skimmings from galvanizers' flux to produce materials useful in replenishing the flux, a process which comprises leaching the skimmings with water so as to make a strong solution of zinc and ammonium chlorids, treating said solution with ammonia, crystallizing diammoniated zinc chlorid from the treated solution with separation of a mother liquor, concentrating the mother liquor by heating it until the temperature of the liquor is about 119° C., cooling the concentrated liquor and depositing crystals of a double salt of zinc and ammonium chlorid in a molecular ratio of 1:3 with separation of a second mother liquor, then concentrating said second mother liquor at a temperature about 130° C. and cooling to deposit crystals of a double salt of zinc and ammonium chlorid in a molecular ratio of 1:2.

15. In the utilization of galvanizers' sal-ammoniac waste to recover therefrom material useful as a galvanizers' flux, a process which comprises leaching the galvanizers' waste with water to obtain a solution containing zinc chlorid and ammonium chlorid in a molecular ratio approximating 1:1, concentrating said solution by heating it until the solution is at a temperature of about 130° C., cooling the concentrated solution and depositing crystals of a double salt of zinc and ammonium chlorids in a molecular ratio of 1:2.

16. In the utilization of galvanizers' sal-ammoniac waste to recover therefrom a material useful as a galvanizers' flux, a process which comprises leaching the waste with water to obtain a solution of zinc and ammonium chlorids in a molecular ratio about 1:1, adding ammonium chlorid to bring the molecular ratio to about 1:2, concentrating the solution at about 119° C. and cooling the concentrated solution so as to deposit crystals of a double salt of zinc and ammonium chlorid in a molecular ratio of 1:3.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 36, for "powder" read power; and same page and column, line 44, strike out the syllable and words "ter has been evaporated and 22 pounds of" and insert instead diammoniated salt and either the 1: 2 or; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of September, A. D. 1935.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.