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SALT BATH RECTIFIER

Edward N. Case, Philadelphia, Pa., assignor to
American Cyanamid Company, New York,
N. Y., a corporation of Maine

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This invention relates to heat treatment of ferrous metal articles, and more particularly, to such heat treatment by means of fused salt baths.

Heat treating operations for articles of various metals are often carried out by immersing the metal article to be treated in a fused salt bath. This method of heat treatment is advantageous because of the rapid transfer of heat from the salt bath to the metal articles, thus providing a rapid process well adapted to large scale production. However, difficulties are sometimes experienced in heat treating steel and other ferrous metal articles in fused salt baths because the salt baths usually cause more or less decarburization of the metal surface. Heretofore this decarburizing effect has been overcome by introducing a carburizing material, for example, an alkali metal cyanide or other cyanogen compounds, into the fused salt bath. By this method the carburization which occurs more or less compensates for the decarburizing effect of the bath. However, in commercial work it is practically impossible to continuously maintain a bath in a substantially neutral condition, that is, in such a condition that the net effect is neither carburization nor decarburization. If the amount of carburizing material is exactly proportioned so that the carburizing effect equals the decarburizing effect, the carburizing power of the bath soon decreases with use and the steel then becomes decarburized. Upon the addition of more cyanide, the bath becomes carburizing and the ferrous metal articles introduced into the same are case carburized. Obviously, the use of such carburizing materials for the purpose of offsetting the decarburizing tendency of the bath is not an entirely satisfactory solution, since a "neutral" bath, that is, one which would eliminate the decarburizing tendency without introducing carburizing activity, would be far more preferable.

This problem is somewhat less serious when the articles to be treated are of relatively massive proportions and the time of heat treatment is relatively short. However, this tendency of the salt baths to decarburize steel and other ferrous metal articles has heretofore made the salt bath method unsuited for practicable heat treatment of thin steel articles, such as steel sheet or steel wire, except for treatments of very short duration. For example, when a thin steel sheet is heat treated in a salt bath which has a decarburizing action, the sheet is very rapidly and almost completely decarburized throughout its depth, thus producing a sheet of entirely differ-

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ent characteristics than that desired. On the other hand, when cyanide is added to the bath for heat treating a steel sheet, the small amount of carburization which occurs often is sufficient to substantially entirely carburize the sheet throughout. Hence, it has heretofore been impossible to heat treat steel or iron sheet in a fused salt bath without materially changing its carbon content to an undesirable extent. For this reason, steel sheet commonly is heat treated in furnaces, such as muffle furnaces, in stacks. This involves handling the sheets to stack and unstack them, and ordinarily the sheets become coated with oxide scale which often must be removed prior to subsequent use. Also, the stacked sheets often stick together, requiring considerable labor to separate the sheets.

It is an object of this invention to provide a new and improved method for heat treating metal articles in fused salt baths.

Another object of the invention is to provide a satisfactory method for heat treating iron and sheet steel in a fused salt bath.

Still another object is to provide an improved heat treating fused salt bath which is substantially neutral in character, that is, which neither carburizes nor decarburizes steel articles treated therein.

A further object is to provide a process for maintaining a fused salt bath used in the heat treatment of metal articles in a neutral condition with respect to carburization and decarburization.

These and other objects are accomplished in accordance with the discovery of the present invention that an organic compound containing a member of the group consisting of chlorine and phosphorus-oxygen groups may be used as a rectifier for the type of heat treating bath described herein. By "phosphorus-oxygen group" is meant a juxtaposition of phosphorus and oxygen in the organic compound.

Thus, when such a fused salt bath has been employed for a sufficiently long time to impart a decarburizing activity to said bath, the addition of one of the aforementioned organic materials hereinafter referred to as "rectifiers" serves to render the bath neutral and non-decarburizing. Also, when employing a freshly prepared bath of such salts containing such a rectifier, the resultant fused salt bath will be found to be resistant to the development of a decarburizing tendency therein so that the development of such a decarburizing effect will be very much delayed.

A tremendous number of compounds are suit-

able for the process of this invention. Among those most commonly available are the various chloro-substituted aliphatic, aromatic, and heterocyclic organic compounds, as well as the hydrochlorides and phosphates of numerous simple and substituted organic bases.

The guanidine hydrochlorides are typical of the rectifiers that may be employed in the present invention, and include the hydrochlorides of a wide variety of substituted guanidines such as the following:

N,N-dibutylguanidine
N,N-diethylguanidine
N,N-dimethylguanidine
N-dodecylguanidine
N-butylguanidine
N,N'-diisopropylguanidine
N-guanylguanidine
N-cyanoguanidine
N-carbamylguanidine
N-aminoguanidine
N,N'-diphenylguanidine
N,N'-di-o-tolylguanidine
N-phenyl-o-tolylguanidine
N,N,N',N'-tetraphenylguanidine
N,N,N',N'-triphenylguanidine
N,N',N''-triphenylguanidine

The aminotriazine hydrochlorides may be employed as rectifiers in the present invention; examples are the hydrochlorides of the following compounds:

melamine ammeline ammelide

Examples of the wide variety of substituted aminotriazine hydrochlorides which may be employed as rectifiers are the hydrochlorides of the following compounds:

2-butylamino-4,6-diamino-1,3,5-triazine
2-diallylamino-4,6-diamino-1,3,5-triazine
2-dibenzylamino-4,6-diamino-1,3,5-triazine
2-dibutylamino-4,6-diamino-1,3,5-triazine
2-dibutylamino-4-phenylamino-6-amino-1,3,5-triazine
2-dicyanomethylamino-4-diethylamino-6-amino-1,3,5-triazine
2-(2,4-di-p-ethoxyphenyl)amino-4,6-diamino-1,3,5-triazine
2-diethylamino-4,6-diamino-1,3,5-triazine
2,4-diethylamino-4,6-diamino-1,3,5-triazine
2-dimethylamino-4-dodecylamino-6-amino-1,3,5-triazine
2,4-dimethylamino-2,4-diphenylamino-6-amino-1,3,5-triazine
2,4-diphenylamino-6-di(beta-cyanoethyl)amino-1,3,5-triazine
2,4-diphenylamino-6-amino-1,3,5-triazine
2,4,6-hexaethylamino-1,3,5-triazine
2-phenylamino-4-ethylolamino-1,3,5-triazine
2-butylamino-4,6-dicyanomethylamino-1,3,5-triazine
2-dodecylamino-4-dicyanomethylamino-6-amino-1,3,5-triazine
2,4,6-hexaethylamino-1,3,5-triazine

The above substituted aminotriazines are prepared by reacting cyanuric chloride with the appropriate amine or amines. The first chlorine to be replaced is split off at temperatures of the order of 0° C., it being preferable to react ammonia before reacting an amine if an NH₂ group is desired in the triazine structure. The second chlorine is replaced at 35°-50° C., while the third chlorine is replaced at about 100° C. Thus, for example, 2-butylamino-4,6-diamino-1,3,5-triazine is prepared by first reacting cyanuric chloride with two or more equivalents of ammonia in aqueous solution at about 0° C., thereafter raising the temperature to 35°-50° C., isolating the 2,4-diamino-6-chloro-1,3,5-triazine which is then reacted in aqueous solution with one mole of butylamine at reflux temperatures to provide the desired product. In carrying out this general reaction, it is preferred to employ an acceptor for the HCl which is produced by the reaction, excess amine being suitable although it is more economi-

cal to employ a base such as NaOH, KOH, Ca(OH)₂, and the like.

Examples of other substituted aminotriazine hydrochlorides that may be employed as rectifiers are the hydrochlorides of the following compounds:

2-cyanoamino-4,6-diamino-1,3,5-triazine
2-(o-methylphenyl)guanylamino-4,6-diamino-1,3,5-triazine
2-o-phenylguanylamino-4,6-diamino-1,3,5-triazine
2,4-dicarbamylmethylamino-6-laurylamino-1,3,5-triazine

The 2-cyanoamino-4,6-diamino-1,3,5-triazine is prepared by reacting dicyandiamide with dicyanimide, and the guanylamino substituted aminotriazines shown above are prepared therefrom by reaction with methylaniline and aniline hydrochlorides, respectively. The above carbamylmethylamino substituted triazine is prepared by reacting cyanuric chloride with laurylamine to replace one chlorine atom, and thereafter with glycino nitrile to replace the other two chlorine atoms, followed by hydrolysis of the nitrile groups.

Examples of chloro-triazines which may be employed as rectifiers in the invention follow:

25 cyanuric chloride
2,4-diamino-6-chloro-1,3,5-triazine
2-amino-4,6-dichloro-1,3,5-triazine
2-amino-4-dibutylamino-6-chloro-1,3,5-triazine
2-amino-4-di(beta-hydroxyethyl)amino-6-chloro-1,3,5-triazine
2-amino-4-beta-hydroxyethylamino-6-chloro-1,3,5-triazine
2-amino-4-phenylamino-6-chloro-1,3,5-triazine
30 2,4-bis-[di-(beta-cyanoethyl)]amino-6-chloro-1,3,5-triazine
2-butylcyanomethylamino-4,6-dichloro-1,3,5-triazine
2-(4-chloro-6-phenylamino-1,3,5)-triazinylpyridinium chloride
2-cyanomethoxy-4-cyanomethylamino-6-chloro-1,3,5-triazine
35 2-cyanomethylamino-4-amino-6-chloro-1,3,5-triazine
2-cyanomethylamino-4,6-dichloro-1,3,5-triazine
2-cyclohexylcyanomethylamino-4,6-di-chloro-1,3,5-triazine
2-di(beta-cyanoethyl)amino-4,6-dichloro-1,3,5-triazine
2,4-di(beta-cyanoethyl)butylamino-6-chloro-1,3,5-triazine
2,4-dicyanomethylamino-6-chloro-1,3,5-triazine
40 2,4-di-beta-hydroxyethylamino-6-chloro-1,3,5-triazine
2,4-di-octadecylamino-6-chloro-1,3,5-triazine
2,4-di-phenylamino-6-chloro-1,3,5-triazine
2-diphenylamino-4,6-dichloro-1,3,5-triazine
2-dodecylamino-4,6-dichloro-1,3,5-triazine
2-octadecylamino-4,6-dichloro-1,3,5-triazine
2-phenylamino-4,6-dichloro-1,3,5-triazine
2-phenylcyanomethylamino-4,6-dichloro-1,3,5-triazine

45 The amino and substituted-amino chlorotriazines shown above are prepared by treating cyanuric chloride with 1 or 2 moles of ammonia or amine. For example, cyanuric chloride upon being reacted with 1 mole of dibutylamine results in the production of 2-dibutylamino-4,6-chloro-1,3,5-triazine, which is then treated with a mole of ammonia or ammonium hydroxide to provide 2-amino-4-dibutylamino-6-chloro-1,3,5-triazine.

50 Examples of various other chlorine-containing organic compounds that can be used as rectifiers in this invention are:

aceto-chloroglucose
60 acetyl m-phenylene diamine hydrochloride
alpha-benzene hexachloride
chloral hydrate
chloroacetic acid
naphthalene tetrachloride
beta-naphthoyl chloride
65 palmityl chloride
p-phenetidine hydrochloride
phenyl chloroacetate
o-phenylene diamine hydrochloride
uns-phthalyl dichloride
70 pinene hydrochloride
pyridine dihydrochloride
stearyl chloride
succinichlorimide
75 tethamethylammonium chloride

tetraethylammonium chloride
o-tolidine hydrochloride
trichlorobenzene

Among the phosphorus-oxygen containing organic compounds that may be used in the process of this invention, the following are typical:

phosphino benzene
triphenylphosphine oxide
phenoxyl-diphenyl phosphine
methylphosphenic acid
methylenyl-tris-triethylphosphonium hydroxide
trimethylisoamylphosphonium hydroxide
triethylisoamylphosphonium hydroxide
triethylphosphine oxide
triethylmethylphosphine oxide
tripropylphosphine oxide
methylethylphenylphosphine oxide
methylphosphenic acid dichloride
isopropylphosphenic acid
phosphino pentane
monoguanidine phosphate
guanidine ammonium phosphate
diguanidine phosphate
guanidine diethyl pyrophosphate
guanidine sodium phosphate
guanidine hypophosphate
guanylurea phosphate
decamethylene diguanidine phosphate

The rectifiers of the present invention may be admixed with the mixture of alkali metal halides and/or alkaline earth metal halides in preparing such a salt mixture for use as a fused salt bath, or they may be added to such a mixture of salts which has been in use for some time, and in the latter case the addition may be made while such mixture is either solid or fused. The rectifiers of the invention may be added to the fused salt baths alone or in admixture with alkali metal halides and/or alkaline earth metal halides. When adding the rectifiers to such fused salt baths, however, it is preferable to add them in admixture with such halides since this results in a more efficient distribution and use of the rectifiers. The alkali metal halide and/or alkaline earth metal halides used in this latter connection are preferably admixed in the same ratio as obtains in the fused salt bath so as not to alter the composition of such bath. While, as aforementioned, the rectifiers may be added to the bath in amounts as high as those equivalent to 10% by weight of the bath with excellent rectification resulting, it is preferred to employ the rectifiers in such amounts as to be equivalent to 2% or less by weight of the bath since this permits the most efficient utilization of the rectifiers, and an amount equivalent to 1% or less by weight of the bath is even more preferred. Also, the addition of the larger percentages of the rectifiers tends to alter the composition of the bath so that it is preferred to employ the smaller amounts of rectifier when eutectic mixtures are employed in order that there will be no undue alteration of the ratios of alkali metal halides and/or alkaline earth metal halides which must be somewhat precisely maintained in order to obtain a eutectic mixture. With salt mixtures such as those of NaCl and KCl which do not form a eutectic but only a minimum melting point mixture, such precautions are not as necessary, however.

As aforementioned, the type of fused salt bath in which the rectifiers of the present invention are particularly effective is one composed of mixtures of the alkali metal halides and/or alkaline

earth metal halides. Such alkali metal halides are, for example, NaCl, NaF, KCl, KF, LiCl, KIF, RbCl, RbF, CsF, CsCl, and the like. However, the halides of rubidium and cesium being less available are not generally used as a matter of practice. Examples of the alkaline earth metal halides contemplated for use in the present invention are $MgCl_2$, MgF_2 , $CaCl_2$, CaF_2 , $SrCl_2$, SrF_2 , $BaCl_2$, BaF_2 . The present invention contemplates the use of mixtures of the alkali metal halides, mixtures of the alkaline earth metal halides, and mixtures of the alkali metal halides with alkaline earth metal halides, and such mixtures may contain two or more of such halides. The proportions of such halides may be varied over a wide range, but such mixtures should not contain more than 95% or less than 1%, and preferably at least 5%, of a given halide. It is preferred, however, that the salts be admixed in such proportions as to provide a minimum melting point mixture or a eutectic mixture, i. e., a mixture of two or more of the aforementioned halides which has a lower constant melting point than any other mixture of its constituents. Examples of such eutectic mixtures follow:

LiCl 45%, KCl 55%, M. P. 666° F.
 $BaCl_2$ 31%, $CaCl_2$ 48%, NaCl 21%, M. P. 806° F.
 $CaCl_2$ 66.5%, KCl 5.2%, NaCl 28.3%, M. P. 939° F.
 $CaCl_2$ 67%, NaCl 33%, M. P. 941° F.
 $BaCl_2$ 48.1%, KCl 30.7%, NaCl 21.2%, M. P. 1026° F.
NaCl 27%, $SrCl_2$ 73%, M. P. 1049° F.
 $BaCl_2$ 35.7%, $CaCl_2$ 50.7%, $SrCl_2$ 13.6%, M. P. 1110° F.
 $BaCl_2$ 50.3%, $CaCl_2$ 49.7%, M. P. 1112° F.
 $CaCl_2$ 81%, KCl 19%, M. P. 1184° F.
 $BaCl_2$ 70.3%, NaCl 29.7%, M. P. 1209° F.
KCl 61%, KF 39%, M. P. 1121° F.
NaCl 72.6%, NaF 27.4%, M. P. 1247° F.
 BaF_2 70%, CaF_2 15%, MgF_2 15%, M. P. 1454° F.
 $BaCl_2$ 83%, BaF_2 17%, M. P. 1551° F.
 CaF_2 48%, MgF_2 52%, M. P. 1738° F.

Of the various alkali metal halide and/or alkaline earth metal halide baths, it is preferred to employ those of NaCl and KCl, $BaCl_2$, NaCl and KCl and $CaCl_2$, NaCl and KCl, most preferably in eutectic or minimum melting point mixtures.

Examples of other halide mixtures which may be employed in connection with the present invention, but which are not eutectic mixtures, follow:

KCl 56%, NaCl 44%, M. P. 1220° F.
KCl 50%, NaCl 50%, M. P. 1224° F.
NaCl 22%, $BaCl_2$ 55%, KCl 23%, M. P. 1020° F.

While the salt bath mixtures shown above are largely used in the preparation of the so-called "medium temperature" (1000°-1750° F.) baths, and to some extent in the "low temperature" (300°-1000° F.) baths, other alkali metal halide and/or alkaline earth metal halide mixtures may be prepared for use in "high temperature" (1750°-2400° F.) metal treating baths. An example of such a bath is one containing 10% NaCl and 90% $CaCl_2$. Such high temperature baths are not eutectics and are sometimes referred to as "glasses." In addition to the $CaCl_2$ -NaCl bath mentioned above, such high temperature baths have also been prepared using 90% $BaCl_2$ and 10% NaCl. However, it is preferred to employ the rectifiers in conjunction with the medium and low temperature baths since their effectiveness is greatest at such temperatures and with such baths. When using such high temperature baths, it is generally necessary to preheat the work for immersion therein and the aforementioned medium salt baths may be used in this connection.

The composition of steel pots used to contain the fused salt bath contemplated by the present invention may vary from cast iron and low car-

bon steels to more corrosion resistant high chromium and nickel alloys. The welded or cast chrome-nickel containers are preferable. Ceramic containers are still more preferable when using the fused salt mixtures contemplated by the present invention. Such ceramic pots are usually made of refractory materials consisting of silica, oxides and silicates of magnesium, calcium and aluminum, the salt mixtures contained therein being heated by immersed heating units such as enclosed resistors or electrodes, instead of by the usual gas or oil-fired installations. Direct resistance electrode heaters are also employed, particularly in large installations.

The advantages of the process of the invention as compared with prior processes reside mainly in that the excess rectifier does not result in the bath becoming carburizing and that, hence, there is no difficulty in adjusting or maintaining the bath in the desired neutral condition. Further, only small additions of the neutralizer are required so that there is no build up of impurities within the bath. In fact, the percentage of the addition of the neutralizing material required is well below the losses resulting from "drag out" which is due to the adherence of the

fiers of the invention are employed in conjunction with fused salt baths in the treatment of metal articles.

EXAMPLE 1

16 lbs. of sodium chloride, 16 lbs. of potassium chloride, and 0.3 lbs. of cyanuric chloride were thoroughly admixed. 6 lbs. of this mixture were melted in a pressed steel pot. As the salt mixture reached 300° F., obnoxious fumes were given off. On reaching 1600° F. the evolution of such fumes had ceased. The bath was quiet and clear with small particles moving in it. Samples were taken and tested for alkalinity and none was found. 1/4-inch drill rod and high and low carbon steel sheet samples were treated in the bath for various periods of time at temperatures of 1500°-1600° F., and brine quenched (10% NaCl solution) to determine any change in carbon content. Such change was detected by chemical analysis of the carbon sheet and by hardness measurements on the drill rods. Results obtained on the hardness measurements of the drill rods are summarized in Table I in which R_c and R_{15N} are Rockwell hardness values taken on the C and 15N scales, respectively.

Table I

Age of Bath, Hrs.	Hardness						Remarks
	R _c After—			R _{15N} After—			
	10 min.	20 min.	30 min.	10 min.	20 min.	30 min.	
0-----	64	64	64	92.5	92-5	92.5-3	Overnight at 1000° F Add 1% salts. Add 1% fresh salts.
1-----	64.5-6	63	64-.5	92.5-3	92-3	92-.5	
18-----	64-5	65	65	91-3	92	92-3	
22-----	65	65	65	91-2.5	92-3	92.5	
23-----	65	64-5	65	92-.5	90-2	92.5-3	

fused salt to the work. In this connection, the rectifiers are usually added to the bath in an amount within from 0.01-10% of the weight of the bath. Highly satisfactory results are obtained, however, by employing additions which

The results obtained by chemical analysis of the carbon sheets are summarized in Table II. The low carbon steel sheets analyzed 0.06% C, while the high carbon sheets analyzed 1.06% C before treatment.

Table II

Date	Time	Remarks	Low C Steel After—		High C Steel After—	
			10 min., Per Cent C	30 min., Per Cent C	10 min., Per Cent C	30 min., Per Cent C
21	3 p. m.	Idle overnight at 1000° F.	.15	.12	.86	.87
	4 p. m.		.12	.13	.95	.87
22	9:30 a. m.	Desludge; add 1% new salts.	.04	.06	.95	.85
	1 p. m.	Add 1% new salts.	.07	.07	.95	.85
	2:30 p. m.		.07	.09	.92	.81

are considerably less than 1% so that it is preferred to add an amount of rectifier that is from 0.01-1.0% of the weight of the bath. In addition, it has been found that a rectifier employed in the process does not result in any nitriding, so that the bath is also maintained neutral in this respect. The use of the process of the present invention is particularly advantageous in connection with low carbon shim stock which is especially susceptible to carburization upon being immersed in a fresh bath containing carburizing agent or a bath to which recent large additions of fresh salts and carburizing agent have been made.

The following examples are submitted as being illustrative of the manner in which the recti-

EXAMPLE 2

A mixture of 10 lbs. of sodium chloride, 10 lbs. of potassium chloride, and 3 oz. of guanidine hydrochloride was prepared. 6 lbs. of this mixture were melted in a pressed steel pot, melting at about 1224° F. 1/4-inch drill rods and high and low carbon steel sheets were treated in the bath for various periods of time at temperatures of 1500°-1600° F. to determine any change in carbon content and hardness. Change in carbon content was determined by chemical analysis of the steel sheet and hardness measurements were made with a Rockwell hardness tester on the drill rods as in Example 1. The results obtained on the drill rods treated in this bath are summarized in

Table III.

Table III

Age of Bath, Hrs.	R _o After—			R _{15N} After—			Remarks
	10 min.	20 min.	30 min.	10 min.	20 min.	30 min.	
0-----	64.5-66	64	64-5	92-.5	92-.7	91.5-2.5	Idle overnight at 1160° F. Add 1% new salts.
1-----	64	64	64	92-3	92.5-3	92.5-3	
18-----	63.5-4	63.5-4	63.5-4	92-.5	91.5-2.5	92-.5	
21-----	63.5-4	64	63.5-4	92-3	92-.5	91.5-3	Idle at 1150° F. No additions. Add 1% new salts. Add 5% new salts.
22-----	64-5	64-5	64-5	91-2	93-4	92-.5	
70-----	64.5-5	64.5-5	62-5	91-3	93-4	92-3.5	
71-----	65-6	64-5	64-5	92.5-3	93.5-4.5	93.5	
72-----	64.5	64-5	64-5	90-4	92.5-3.5	93-4	

Changes in carbon content of the steel sheets as determined by analysis are summarized in Table IV. The low carbon steel sheets analyzed 0.09% C and 0.014% N, and the high carbon steel sheets analyzed 0.85% C and 0.013% N before treatment.

EXAMPLE 4

A molten salt bath was made up using a steel pot 14 in. deep and 8 in. inner diameter. The pot was filled with a salt mixture consisting of 49.5% sodium chloride, 49.5% potassium chloride, and 1% diguanidine phosphate, the latter being

Table IV

Date	Time	Remarks	Low C Steel After—				High C Steel After—			
			10 min.		30 min.		10 min.		30 min.	
			Per cent C	Per cent N	Per cent C	Per cent N	Per cent C	Per cent N	Per cent C	Per cent N
26-----	3 p. m.		.16	.066	.13	.094	.87	.020	.78	.025
	4 p. m.		.11	.034	.10	.062	.89	.015	.90	.025
27-----	9:40-----	Idle overnight at 1160° F. Desludge, add 1% new salts.	.11		.09	.087	.91		.86	.025
	1:10-----	do-----	.07		.10		.91		.87	
	2:00-----	do-----	.12		.16		.91		.78	
30-----	12:30-----	Bath idles at 1150° F. till	.07		.11		.92		.85	
	1:30-----	Desludge, remove 1% salts, add 1% new salts.	.05		.14		.92		.84	
	2:30-----	Add approximately 3% new salts.	.12		.18		.87		.84	

EXAMPLE 3

A salt bath which was originally made up of equal parts of sodium and potassium chlorides and had been used for a long period of time so that it was strongly decarburizing was melted in a pressed steel pot. Considerable sludge was present, but being in a fine particle state could not be removed. Steel sheets of 0.09% and 0.85% carbon content were treated in this bath at 1500° F. for various periods of time and after the addition of various amounts of guanidine hydrochloride. Changes in carbon content of the steel sheets were determined by analysis and the results are summarized in Table V. On the addition of guanidine hydrochloride, the salt appeared to vaporize instantly and go up in a white smoke. The bath became slightly cloudy but cleared after a while.

the rectifier. The bath was held at the temperature 1500° F., and round test pieces of SAE 1040 steel and ½ in. and ¼ in. round test pieces of drill rod were held in the bath for 30 minutes and for 1 hour, brine-quenched, and tested for hardness both on the Rockwell-C and Rockwell-15N scales and with a test file. Low carbon shim stocks (0.06% C) were held in the bath for 10, 30, and 60 minutes, to determine the degree of carburizing activity of the bath. Pieces of high carbon, thin sheet steel (0.008 inch analyzing 0.93% C) were also held at various occasions in the bath for the same periods of time to determine the decarburizing tendencies of the bath. One-inch bars of drill rod were treated for various periods of time to determine the depth of decarburization by chemical analysis of 0.004 inch layers of steel. The data obtained on the above experiments is summarized in Tables VI and VII.

Table V

Date	Remarks	Alkalinity as Per cent Na ₂ CO ₃	Low C Steel After—		High C Steel After—	
			10 min., Per cent C	30 min., Per cent C	10 min., Per cent C	30 min., Per cent C
27-----	Heavy sludge at bottom	0.13	.08		.52	
	Add .1% rectifier	none				.59
	Add .5% rectifier	0.08	.06	.08	.73	.55
28-----	Idle 2 hours		.08		.83	.67
	Idle overnight at 1300° F.					
	20 hours later	0.17	.06		.81	.67

Table VI

[1 hour at 1500° F. in neutral bath.]

Date	Per Cent C of shim stock ¹	R. Hardness	
		SAE 1040	Drill Rod
3/6	1.31	52	62-64
3/6	0.96	57.3	64-65
3/10	0.87		
3/11	0.86		
3/12	0.89	53-57	65-66
3/12	0.88	50-53	65-66
3/15	0.91	44-45	64-65

¹ Originally 0.93% C.

TABLE VII

[Decarburization on 1 inch O. D. drill rod bars.] (3)

Bar No.	D-3		D-4 ¹		D-5 ²		D-2		F-1	
Temp.-Time	1500-18 hrs.		1 hr.		1 hr.		2 hrs.		1600° F.-1 hr.	
Cut.	in.	Per Cent C	in.	Per Cent C	in.	Per Cent C	in.	Per Cent C	in.	Per Cent C
1	.0018	.65	.0015	1.02	.002	0.97	.002	1.00	.002	0.86
2	.0056	.70	.0048	1.00	.006	0.97	.0058	.99	.006	0.92
3	.009	.74			.010	0.98			.010	0.94
4					.014	1.00				

¹ After 24 hours without addition of fresh salts.² After addition of fresh salts, 5% of the bath.

It will be noted that the bath rectified with guanidine phosphate decarburizes less than the baths mentioned in Examples 1, 2, and 3. Furthermore, it has been observed that guanidine phosphate corrodes the work treated and the bath pot less than the baths of the previous examples, and guanidine phosphate is a preferred rectifier for the compositions and methods of this invention.

The data shown above in connection with the examples which deal particularly with hardness measurements provide definite indication that the degree of hardness imparted to the work is maintained at the same high level as the baths continue to be used, provided the rectifiers of the invention are employed from time to time. The R_c values shown above correspond to the R_{15N} values, thus showing that the degree of hardness obtaining near the surface of the metal article is uniform.

While the data shown in the above examples with regard to the change in carbon content of the steel sheet resulting from treatment in the fused salt baths show that change does occur, such is negligible as compared with that which occurs when such articles are treated in baths with which no rectifier is employed. Also, it will be noted that the carbon content of the treated articles is maintained at a fairly constant level which is no appreciably altered by variations in the time of treatment, by continued use of the bath, or by the addition of a rectifier or fresh salts containing a rectifier. It is likewise obvious both from the data with regard to hardness and with those concerning the carbon content of the work treated that the addition of new salts required to maintain the bath in a neutral condition would be well below the amounts lost due to drag out. This considerably extends the period over which a given bath can be used continuously.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and re-

stricted solely by the scope of the appended claims.

This application is a continuation-in-part application Serial No. 778,471, filed October 7, 1947, now abandoned.

I claim:

1. A salt mixture for use in preparing a salt bath, said mixture comprising 0.01-10.0% of an organo nitrogen compound of the group consisting of a guanidine hydrochloride, a guanidine phosphate, a chloro triazine, and an amino triazine hydrochloride, the remainder of said mixture being a mixture of at least two members of the group consisting of an alkali metal halide and

an alkaline earth metal halide, said halide mixture containing at least 1% but less than 95% of a given halide.

2. The salt mixture of claim 1, in which the organo nitrogen compound is present in an amount ranging from about 0.01-2.0%, in which the halide mixture is substantially a minimum melting point mixture.

3. A salt mixture for use in preparing a fused salt bath, said mixture comprising from 0.01-1.0% of a guanidine phosphate, the remainder of such mixture being a mixture of sodium chloride and potassium chloride containing at least 40% and less than 60% of either chloride.

4. A salt mixture for use in preparing a fused salt bath which comprises from 0.01-1.0% of a guanidine hydrochloride, the remainder of such mixture being a mixture of sodium chloride and potassium chloride containing at least 40% and less than 60% of either chloride.

5. A salt mixture for use in preparing a fused salt bath which comprises from 0.01-1.0% of melamine hydrochloride, the remainder of such mixture being a mixture of sodium chloride and potassium chloride containing at least 40% and less than 60% of either chloride.

6. The mixture according to claim 1 in which the solid organic substance contains the guanidinium radical.

7. A fused salt bath for heat treating ferrous metals which comprises 0.01-10.0% of an organo nitrogen compound of the group consisting of a guanidine hydrochloride, a guanidine phosphate, a chloro triazine, and an amino triazine hydrochloride, the remainder of said bath being a mixture of at least two members of the group consisting of an alkali metal halide and an alkaline earth metal halide, said halide mixture containing at least 1% but less than 95% of a given halide.

8. The fused salt bath of claim 7 in which the halide mixture is substantially a minimum melting point mixture and in which the solid organic substance has been added in an amount from 0.01-2.0% of the weight of the bath.

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9. A fused salt bath for heat treating ferrous metal articles which comprises a mixture of sodium chloride and potassium chloride, said mixture containing at least 40% and less than 60% of either chloride, to which has been added 5 0.01-1.0% by weight of the bath of a guanidine phosphate.

10. A fused salt bath for heat treating ferrous metal articles which comprises a mixture of sodium chloride and potassium chloride, said mixture containing at least 40% and less than 60% of either chloride, to which has been added from 10

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0.01-1.0% by weight of the bath of guanidine hydrochloride.

11. A fused salt bath for heat treating ferrous metal articles which comprises a mixture of sodium chloride and potassium chloride, said mixture containing at least 40% and less than 60% of either chloride, and to which has been added from 0.01-1.0% by weight of the bath of melamine hydrochloride.

EDWARD N. CASE.

No references cited.