HEAT TREATMENT OF INDUSTRIAL MATERIALS IN MOLTEN SALTS

R. W. Foreman

Park Chemical Company
8074 Military Ave.
Detroit, Michigan 48204

A wide variety of industrial heat treating is performed in molten salts. Processing of metals includes surface hardening, brazing, annealing, coloring, descaling, and metals recovery. Nonmetallics processing includes elastomer and plastic curing, glass tempering, and plastics molding. An involved technology covering both salt and materials properties and engineering surrounds these applications. Selected examples are discussed in detail in this presentation.
Molten salts are used for heat treating a wide variety of industrial materials. Metals are the dominant material with ferrous alloys most important but curing of elastomers and plastics, and tempering of glass have been growing in recent years. Industrial use of molten salts began back in the 1860's with the carburizing of steel using molten sodium cyanide. This remained the major use until after W.W.I when neutral salts for through hardening steel and tool steels came into use. Other uses have been added in the ensuing years for such purposes as annealing steels and other non-ferrous metals, coloring the surface of steels, nitriding steels, brazing aluminum and steels, and surface cleaning of steel plus other metals. The curing of rubber and plastics and the chemical tempering of glass have been more recent applications of molten salts.

While the exact usage level is unknown, rough estimates are that upwards of 50,000,000 lbs. per year are consumed in North America for industrial heat treating.

The attractiveness of salt for heat treating stems from several favorable features. These are as follows: (1) Rapid heat up time. Salts have a high K factor and will heat up materials 4-5 times more rapidly than they can be heated in gaseous media or vacuum. (2) The heating is extremely uniform since the salt coats the entire surface and the conductivity is high. (3) Salts are capable of very precise temperature control commonly to within a degree or two centigrade. (4) Salts are relatively dense and thus provide a buoyancy effect on parts being heat treated. This minimizes distortion. (5) Salts offer a protective medium for heat treating whereas air oxidizes surfaces severely. (6) Salt has a relatively high heat capacity and thus a large amount of heat can be stored in a relatively compact space. (7) Salt is one of the most effective ways to achieve selective heat treating by partial immersion not readily done by other techniques. (8) Finally, salt is highly energy efficient and can offer significant energy savings over alternate methods of heat treating.

Salt is not without its disadvantages. Under some circumstances salt can be more corrosive towards surfaces than vacuum or inert gas atmosphere. Salt can also pose problems in removal after heat treat particularly from blind holes or highly recessed areas. Third, salt presents a potential pollution and disposal problem. However, the technology for dealing with this is well advanced and need not be a deterrent. The emphasis in this paper will be on applications of molten salts. These will be covered in approximate order of their current industrial importance as measured by the volume of salt used.
for that purpose. These applications are listed in Table I.

TABLE I
Salt Bath Heat Treating: Applications

| Application                        | Salt Bath Method          |
|------------------------------------|---------------------------|
| Neutral Hardening of Steel         | Austenitize               |
| Ha-Speed Steel Hardening           | Marquench/Ausquench       |
| Liquid Carburizing                 | Solution treating         |
| Liquid Nitriding                   | Quenching                 |
| Liquid Nitriding                   | Tempering                 |
| Aluminum Dip Brazing               | Cyanide based             |
| Aluminum Solution Treating         | Non-cyanide based         |
| Miscellaneous                      | Tool Steel "Casing"       |
|                                   | Ductile nitriding         |
|                                   | SS Annealing              |
|                                   | Copper/Brass Brazing      |
|                                   | Ausbay Quenching          |
|                                   | Copper Annealing          |
|                                   | WC Brazing                |

Before proceeding to the actual applications it would be of use to discuss the equipment used for heat treating. There are a wide variety of salt bath designs which are used in industry. The earliest designs were based on gas or oil fired pots that were inserted in firing chambers usually built of brick. The more modern heat treating facilities utilize electrically heated pots at lower temperatures. These are quite often heated by resistance heaters either internally or externally located. A typical low temperature resistance heated type of pot is shown in Figure 1. (Note: the figures will all be at the end of the talk) For higher temperature applications above about 500°C. It is common to use direct resistance heating of the salt in either metal lined or more commonly ceramic lined baths that are usually constructed in the square or rectangular configuration. The two most common used salt baths designs are illustrated in Figures 2 and 3. Figure 2 illustrates an over-the-side type electrode arrangement and Figure 3 illustrates the submerged electrode arrangement. The over-the-side electrode has the advantage of being easily removed and replaced when electrodes become worn or damaged but has a disadvantage that it consumes a fair amount of the working space in the bath and is also a little less efficient. The submerged electrode type bath allows the greatest working volume in the bath and is the most energy efficient design. It has the disadvantage that when repairs or replacement are needed a substantial rebuilding
The major use of molten salts is for the neutral hardening of low to medium alloy steels containing medium to high carbon. To understand the accomplishments of this process one needs to have a background in the metallurgy of steel and particularly in the microstructural forms of steel which are important to its relative hardness. Figure 4 shows an iso-thermal transformation diagram, sometimes called a time temperature transformation diagram for a typical medium carbon low alloy steel. The purpose of neutral hardening is to cool (quench) steel from high temperature rapidly to low temperatures then hold it at that temperature more or less iso-thermally to permit transformation of the steel to relatively hard structures. One of the harder structures is known as Bainite and the hardest of all is Martensite. The industrial terms used for this are Aus-Tempering or Ausquenching when it is a Bainitic structure that is desired and Martempering or Refquenching when it is a Martensitic structure that is desired. The quenching is generally done from a high temperature neutral salt down to a low temperature nitrate based salt. This must be done rapidly enough to avoid transformation to softer structures that are commonly referred to as Pearlite. At the higher elevated temperature the steel exists in a form known as Austenite and will transform rapidly at the lower temperatures to other forms as shown in the time temperature transformation diagram. The time scale here is logarithmic so the amount of time that can be tolerated to avoid Pearlitic transformation is very short, often a second or two.

The Austenitizing can be done in atmosphere and quenching in salt though this practice is not as common as the salt to salt type of quenching. There even are a few installations in which the higher temperature is accomplished in salt and the quenching done in a medium such as water or oil, but these are relatively unusual.

The types of salt baths that are used for Austenitizing are commonly referred to as neutral salts. The composition, operating range, and the commonly encountered chemical reactions in this type of bath are shown in Table II.

TABLE II

Austenitizing Salt Baths

| Operating Range: | 760-1000°C |
|------------------|------------|
| Composition:     | NaCl/KCl/BaCl₂ (optional) |
| Decomposition:   | NaCl + O₂ → Na₂O + Cl₂ |
| Contaminants:     | Metallics, refractories, carbon, nitrate |
The operating temperature range indicated is readily accomplished in mixtures of sodium and potassium chloride for up to temperatures of about 875°C. If higher temperatures than this are required, it is common to add barium chloride to the mixture to lend it greater stability. The volatility of sodium and potassium chloride increases substantially at temperatures above 900°C, leading to excessive fuming. Also, the higher the temperature, the more tendency for the reaction of the chloride with the oxides on the metals to produce metallic chlorides and sodium or barium oxides. The latter are powerful decarburing agents even at relatively small concentrations. An important aspect of the use of this type of bath is that either a counteractant or preferably a chemical reversal of this reaction is needed and commonly used.

The quench salt baths commonly in use are outlined in Table III.

**TABLE III**

**Quench Salt Baths**

| Operating Range: | 150-400°C |
|------------------|-----------|
| Composition:     | NH₄Cl, NaNO₃, NaNO₂ |
| Decomposition:   | NaNO₂ → Na₂O + CO₂ + Na₂CO₃ |
| Contaminants:    | Cl⁻, CO₃⁻, Metallics |
| H₂O Addition:    | Low levels effective |
| Control:         | Physical: Electrical Conductivity |
|                  | Thermal Conductivity |
|                  | Melting Point |
|                  | Wt. Loss on Drying |
|                  | Chemical: Acid Titration (O²⁻, CO₃²⁻) |
|                  | AgNO₃ Titration (Cl⁻) |

461
The composition of these salts is sodium and potassium nitrate with sodium nitrite commonly added. The higher the nitrite level in the salt up to about 50% the lower the melting point of that salt will be. Thus the first basis for choice of salt composition is the operating temperature that is to be used. One uses as high a melting point as one can comfortably work with since the economics and the thermal stability favor the lower nitrite, higher nitrate containing salts. The chemical changes that take place in this type of salt are numerous but the most commonly encountered problem is the accumulation of chlorides from carry-over from the austenitizing baths. These will build up and become supersaturated in the quench salt. They must be removed to maintain effective quenching. A common practice here is to crystalize out the excess chlorides and remove them by sludging or screening procedure. The formation of some sodium oxide and thus eventually carbonate can also take place though this will vary greatly with the particular type of operation. It can be readily counteracted through the use of a liquid nitrate rectifier that reacts sodium oxide and carbonate back to nitrates.

The type of equipment that is used for neutral hardening has evolved from relatively small manual transfer operations to semi-automatic and fully automatic systems. In the semi-automatic systems, parts are handled in fixtures that are transferred by over-head cranes and salt baths and wash lines are arranged in sequence. The most modern types of neutral hardening lines are capable of handling up to 2000 pounds per hour in highly automated hydraulically lifted baskets and fixtures transferred in time and sequences that are controlled by computers. Such systems are fully enclosed with good ventilation and in some cases have salt recovery systems.

The second most commonly used process that utilizes salt baths is that involving heat treatment of tool steels. Tool steel heat treating is somewhat similar to neutral hardening but tool steels are generally higher alloy and include high speed steels that contain several alloying elements such as molybdenum, chromium, nickel, cobalt, vanadium as well as carbon. In order to harden high speed steels it is necessary to heat them to
higher temperatures than are commonly used in neutral hardening. To minimize the thermal stresses and to obtain the very short exposure time at high temperatures it is common practice to preheat in two stages. Following the solution treating at the high temperature, the tools are quenched at intermediate temperatures such as 500°C to stabilize them in the austenitic condition. They are then cooled down relatively slowly to achieve martensitic transformation. They are then taken back up for tempering sometimes two and three times for secondary hardening and to relieve stresses. The sequence and the types of baths and the temperatures ranges used commonly for high speed tool steels are shown in the Table IV.

**TABLE IV**

| OPERATION       | TEMP. RANGE °C | COMPOSITION                                      |
|-----------------|----------------|--------------------------------------------------|
| Preheat (one or two stage) | 650-930       | NaCl, KCl, BaCl₂                                 |
| High Heat       | 930-710        | BaCl₂, NaCl (SiO₂)                               |
| Quench          | 540-650        | 1. BaCl₂, NaCl, CaCl₂                            |
|                 |                | 2. Na₂CO₃, KCl, NaCN                             |
| Temper          | 290-590        | Two Types:                                       |
|                 |                | 1. KO₂₃, NaNO₃                                   |
|                 |                | 2. BaCl₂, NaCl, CaCl₂, KCl                       |

The kinds of salt baths used are neutral salts that are very similar to those used for neutral hardening. The high heat is generally based on barium chloride or barium chloride with a small addition of sodium chloride. Barium chloride has the highest thermal stability and lowest volatility of commonly available chloride salts. The quench salt baths are commonly a neutral salt but in order to get low enough melting and fluidity ranges, these salts generally have calcium chloride added along with sodium, potassium and barium chlorides.

The kind of equipment used for tool steel hardening parallels closely that used for neutral hardening though often special designs are used where very large parts such as broaches or rolls are heat treated. There are some automated tool steel lines though not as many as used in neutral hardening.

The next most commonly used salt bath processes involve surface treatments of which carburizing is the most common with li-
quid nitriding gaining increasing favor. Table V shows the types of salt baths that are used for liquid carburizing with the operating temperatures and salient features.

**TABLE V**  
**Liquid Carburizing Processes**

| Temp. (°C): | Cyaniding | Light Case | Deep Case | Non Cyanide |
|-------------|-----------|------------|-----------|-------------|
|             | 760-840   | 815-900    | 870-950   | 870-980     |
| Time (hrs.):| <1        | .5-3       | 1-6       | .3-10       |
| Case Depths (mils): | 1-10 | 5.35 | 15-60 | 5.150 |
| Case Compos’n: | C & N | C+Some N | Nearly all C | All C |
| Carbon Cover: | Little or None | Light | Heavy | Moderate (agitated) |
| Average Operating % | 30 | 20 | 10 | 0 |

The most interesting of these processes today is the non-cyanide based carburizing process which has been in commercial use for less than 10 years. Table VI shows the details of the non-cyanide carburizing process. The salt bath consists of an equimolar mixture of sodium carbonate and potassium chloride into which is stirred relatively pure carbon under controlled conditions.

**TABLE VI**  
**Non-Cyanide Carburizing Salt Baths**

| Composition: | Alkali Carbonates/Chlorides-Proprietary Carbon |
|--------------|-----------------------------------------------|
| Decomposition: | None                                           |
| Contaminants: | Metallics (Fe), SiO₂/Al₂O₃                     |
| Maintenance: | Cover replenishment                            |
| Control:      | Physical: CI012 Test Piece hardness; Chemical: H₂O insolubles (%C) |
| Correction:   | Add Carbon Adjust Agitation Sludge             |
The rest of the details are shown in Table VI. This process is probably the most economic means for carburizing steel presently available in industry. The equipment used is very similar to the neutral hardening baths shown earlier but with important differences. The bath is operated with a layer of relatively pure carbon on the surface which requires a relatively low rpm agitator to stir the carbon into the bath on a continuing basis. The rates of carburizing are comparable to other processes and are primarily diffusion controlled. The choices of post treatment after carburizing are broader with this process than with cyanide base salts. For example, one can quench directly into nitrate salts which is unsafe with cyanide salts.

There are several commercial nitriding processes as outlined in Table VII which depend on alkali cyanates as the active ingredient.

### TABLE VII

**Liquid Nitriding Processes**

|                | Conventional (Alloy Steels) | Cyanide "Ductile" | Non-Cyanide "Ductile" (Low alloy steels) |
|----------------|-----------------------------|-------------------|----------------------------------------|
| Temp. (°F)     | 540 570°C                   | 570°C             | 650°C                                  |
| Time (hrs.)    | 1-1.0                       | 5-3.0             | 5-3.0                                  |
| Case Depths (mils) | .5-1.5                     | 15/30             | 15/30                                  |
| Case Composition | Fe₂N                       | Fe₂N + Diffused N | Fe₂N + Diffused N                     |
|                |                             |                   | (Fe₃N in Some)                         |
| Average Operating % NaCN/% NaCNO | 30/15                     | 40/50             | < 4/50                                 |

The various proprietary processes differ in how the cyanate is generated. From many years this was done by oxidation of cyanide ion and many such baths are still in use. The cyanate ion reacts with the steel to generate an iron nitride surface. If done properly some nitrogen diffuses below the very thin nitride layer at the surface. At very high cyanate ion levels the nitride layer will be less brittle than at relatively lower cyanate ion levels. The non-cyanide or very low cyanide level type nitriding is accomplished in molten salts in which cyanate ion is generated from organic sources, particularly polyurea. Very little cyanate ion exists in these baths and yet the cyanate ion levels are very high.

465
These produce the most effective nitriding in steel. The nitriding of steel is done to produce a very wear resistant surface and has become a popular way of producing smaller size parts which have wide application in the down sizing of engines.

There are many other salt bath processes which have somewhat lesser breadth of application but are deserving of some mention here. Aluminum dip brazing is a means for joining aluminum parts of relatively complex nature through use of an aluminum alloy that melts some 25°C below the base metal. This so called braze alloy can be applied in several forms - powder, sheet or clad on the part itself. By immersion in the salt bath at a very precisely controlled temperature, the braze alloy melts and joins the base metal parts. This process is used in the aerospace and electronics industries especially. The salts as shown in Table VIII are based on sodium and potassium chlorides with fluorides and lithium chloride added.

TABLE VIII

| Aluminum Dip Brazing |
|----------------------|
| Temp: 585-610°C (173°F) |
| Time: 1-3 Min. |
| Equipment: Ceramic Furnaces with submerged or over-the-side Electrodes. |
| Preparation: Alkaline/Acid Dips |
| Preheat to ~1000°F |
| Post Treatment: H₂O Cool & Thorough Wash |

Lithium chloride is a very costly but a very necessary ingredient in this process. It provides both fluidity and fluxing action and enables good brazements to be accomplished.

Another aluminum salt bath process involves solution treating. This is widely practiced in the aerospace industry and increasingly now in those industries moving to lighter weight materials. A good portion of this is done in atmosphere furnaces but salt offers considerably more uniform and rapid heat up and is used where that can be fully appreciated. Table IX lists the key features of salt bath solution treating.

TABLE IX

| Aluminum Solution Treating Salt Baths |
|--------------------------------------|
| Operating Temp: 460-560°C |

466
**TABLE IX (cont.)**

| Composition: | KNO₃, NaNO₃ |
|-------------|--------------|
| Decomposition: | NaNO₃ → Na₂O → Na₂CO₃  
NaNO₃ → NaNO₂ |
| Contaminants: | CO₃⁻, NO₂⁻, metallics, Cl⁻ |
| Control: | Physical: Test Piece ---- IGA  
Chemical: pH/Acid Titration  
NO₂⁻ by KMnO₄ Titr'n.  
H₂O + Acid Insolubles  
Cl⁻ by Ag⁺ Titr'n. |
| Correction: | INR  
Na₂Cr₂O₇  
(SLSR) |

The salts are predominantly sodium and potassium nitrates. Some miscellaneous processes that utilize salt are briefly outlined in Table X.

**TABLE X**

| Miscellaneous Salt Bath Processes |
|----------------------------------|
| **Process** | **Key Salt Bath Features** | **Process Key Control** |
| -------------- | ------------------------- | ----------------------- |
| SS Annealing | Neutral Salts 870-980°C | Maintain Neutral |
| Copper Brazing | Neutral Salts 870-1095°C | Hold Slightly Alkaline |
| Ausbay Quench | Neutral Salt 480°C | Maintain Compos'n Remove Metallics |
| Copper Annealing | Neutral Salts 700-870°C | Maintain Neutral Remove Metallics |
| WC Brazing | Neutral Salts High Heat/Quench | Controlled Alkalinity |

The entries are self-explanatory.

A few non-heat treating type applications are worthy of mention. Most notably are those that involve cleaning salts. These remove undesirable coatings from the metal. For example, high alloy steels,
stainless steels for example, are descaled utilizing salts that are either oxidizing, reducing, or can have electrolysis imposition to assist the cleaning. In this case the scale is either conditioned for later removal by pickling or can be reduced or electrolytically removed in the salt bath.

Another form of cleaning involves removal of organic matter from steel parts such as extrusion dies, which can be rapidly and quickly cleaned in a caustic base salt having some oxidizing power through addition of nitrates. Likewise the removal of paint racks can be accomplished in caustic nitrate mixtures. The devestimation of casting sand from steel castings utilizes a caustic base salt. All of these processes commonly operate at around 500°C. The salts have somewhat different compositions but generally involve caustic, chlorides, and sometimes fluorides and nitrates.

Finally a few non-metallic heat treating processes deserve mention. One of the fastest growing areas for use of salt bath lies is their use for curing elastomers and various heat resistant plastics. A number of extruded rubber parts are immersed in salt baths at temperatures around 200°C to effect a rapid and uniform cure within one to two minutes. This is more economic and produces a more reproducible cure on rubber than ovens or autoclaves. Likewise certain plastics can be foamed and/or cured in direct contact with salt and in some cases by indirect heating where the plastic is cured by immersion of the mold in the molten salt.

Glass can be chemically tempered at around 420°C in potassium nitrate or a potassium plus sodium nitrate mixture. This involves an ion exchange at the surface of the glass to generate a surface under tension. It is widely used now to make ophthalmic glass much stronger than can be accomplished by thermal tempering.

All of these non-metallic heat treating processes utilize nitrate/nitrite mixtures. The principles that apply to quench salts and neutral hardening apply fairly well in this type of application. However, the salt baths themselves are generally in very different designs because of the needs for handling the work going through the bath. Thus a rubber extrusion line might be very long, narrow and be relatively shallow. Immersion type heaters along the length of the bath are usually used.

In conclusion, the use of molten salts for the heat treating industrial products is steadily growing and expanding to new uses and involves a very wide variety of applications. The choice of salts is heavily dependent upon the temperature range in which they operate and in some cases on the chemistry that can be evolved for that particular mixture. The advantages listed earlier in this talk are fully realized in most situations. The disadvantages can be readily overcome through salt recovery, wash water treatment, and proper handling systems.
Figure 1. Typical isothermal quench furnace.
Figure 2. Salt bath furnace featuring a ceramic pot and over-the-top electrodes.
Figure 3. Submerged Electrode Salt Bath Furnaces.
Figure 4.

TTT CURVE

Low Alloy-Medium Carbon Steel