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HEAT TREATING PROCESS

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This invention relates to an improved heat treating process for metals, including alloys, particularly steel, and more particularly to an improved heat treating process using chlorinated biphenyl as the heat treating medium.

The properties of metals, such as iron, copper, nickel, aluminum, magnesium, uranium zinc, gold, silver, lead and tin, and their alloys, can be modified by various known methods of heat treatment which include the heat treating operations known as quenching, annealing and precipitation hardening treatment as well as simple heating baths.

The purpose of the heat-treating of metals is to obtain certain desired properties in the product, such as ductility, hardness or toughness as by alternation of microstructure and mechanical properties or relief of internal stresses.

One of the most common heat treating operations is that involving the quenching of steel in a liquid media. If a steel is heated above the eutectoid transformation range (for example to about 1550° F.), the alpha iron (ferrite) changes to gamma iron. The gamma iron is capable of dissolving the combined carbon of the pearlite, a eutectoid alloy of carbon and iron, forming a solid solution known as austenite. If the metal is quenched (cooled rapidly), the austenite does not have time enough to revert to the normal or pearlite condition when passing through and below the transformation range. Instead, a transition product, usually martensite, is formed. Martensite is hard and brittle and its formation results in lower strength. If, however, the metal is tempered or drawn (heated back to a moderately elevated temperature, say 750° F.), the brittle martensite is decomposed, internal stresses are relieved and intermediate microstructural products of greater plasticity are formed. These intermediate microstructural products possess the combination of strength and toughness usually associated with steel.

Generally common nonferrous metals and alloys do not show allotropic transformations and do not undergo a phase change on cooling, and thus it is generally not possible to harden them by a simple heating and quenching treatment as with steels. Also, in contrast to steels, it is generally not possible to produce grain refinement in nonferrous metals by heat treatment alone.

One method of heat treating nonferrous metals and alloys, known as annealing, comprises heating a nonferrous metal or alloy to a temperature at which grains deformed by cold-work recrystallize to produce new grain. During recrystallization, the hardening effect of cold-working is eliminated and the ductility of the material increases. Once the nonferrous material has recrystallized at the annealing temperature, its properties are unaffected by the rate of cooling, provided that no phase change occurs between the annealing temperature and atmospheric temperature. Heretofore, the cooling after recrystallization has, therefore, been carried out in air.

Furthermore, it is known in the art that certain nonferrous alloys which undergo phase changes can be hardened by a precipitation hardening treatment. For the nonferrous alloy to be liable to such treatment the solubility of an element or compound therein must increase with increasing temperature, and the amount of said element or compound present must exceed its solid-solubility limit at low temperatures. The precipitation hardening treatment consists of heating the nonferrous alloy to a temperature just below the solidification temperature,

holding it at this temperature for a time sufficient to dissolve the phase that precipitates at lower temperatures, and then cooling it rapidly enough to prevent precipitation of the second phase on cooling. On subsequent heating to a lower temperature than that originally used, or by simply letting certain alloys remain at atmospheric temperature, some of the second phase will precipitate from the supersaturated solid solution. At the proper reheating or aging temperature the precipitated particles will be extremely fine and will harden and strengthen the nonferrous alloy. The first step is known in the art as the solution step or solution anneal; the second step is termed the aging step. Up to now it was common practice to execute the rapid cooling of the solution step using a liquid bath as the cooling media.

Still another heat treating operation within the scope of this invention entails subjecting a metal to a hot liquid bath to accomplish various results. The bath is generally maintained at some desired temperature above room temperature. By way of example this would include the annealing of alloy coatings on metals by first contacting the metal article to be treated with a flux (e.g., zinc chloride), passing said metal article through an alloy bath and then through the hot bath maintained, for example, at about 600° F. This results in the annealing of the alloy coating on the metal with any excess alloy being wiped smooth or removed in or just following the hot bath. Another example includes immersion of metal in a bath followed by heating the bath until the metal reaches a desired temperature. The metal can then be removed and allowed to cool or anneal, or it could be subjected to various other operations which require a prior heat-up.

Various media have been employed to effect many of the aforementioned heat treating steps, each of which has its advantages and disadvantages but none of which are completely satisfactory. Thus, although water and water solutions of inorganic salts are the oldest and cheapest heat treating media, and, in the case of steel quenching impart maximum hardenability because they have the highest initial quenching speeds, such media have the disadvantage that the high quenching speeds persist to low temperatures, resulting in warping, distortion, brittleness, uneven hardness and cracking. Also in the heat treatment of iron-containing products such media cause rusting.

To avoid the problems associated with aqueous heat treating media, oil emulsions or various oils such as fish and marine oil, animal oils, mineral oils and their mixtures have been used. Although when used for quenching internal stresses formed during hardening are minimized, quench cracking tendencies are reduced and the rusting problem is greatly minimized, oil, oil emulsions and the like tend to oxidize, form sludge, thicken, break down, and decompose at elevated temperatures, which greatly decreases their useful life as heat treating media and makes them troublesome to use. Also because of these physical and chemical changes, heat treatment in such media produces results which are not uniform. The flammable nature of oils also presents a serious fire hazard in heat treating operations.

Accordingly, the art has long sought for substitutes for oil and water but without much success. It is, therefore, an object of this invention to provide a novel heat treating medium for use in heat treating operations, including but not limited to those described above, which can be used in place of water and oil and oil-based compositions without sacrificing the desirable characteristics of oil which distinguish it from water as a heat treating medium.

It is a further object of this invention to provide a novel and improved quenching medium which provides

the advantages of oil in terms of the quality of quenched articles but which, unlike oil, is extremely fire resistant and is, therefore, more desirable than oil.

It is also an object of this invention to provide a new and useful medium for use in heat treating metals, including alloys, which has no fire hazards or foaming problem and which is substantially uniform in physical and chemical properties over long periods of usage, stable, long lived and can be used within a wide range of temperatures.

A specific object of the present invention is to provide a novel cooling medium useful in the precipitation hardening of non-ferrous materials.

It is also an object of this invention to provide a new and useful medium for use in heating baths which has oxidative and thermal stability, high boiling temperature, low volatility and fire resistance. These and other objects will be apparent to those skilled in the art from the following discussion.

In acordance with the foregoing objects, it has now been found that chlorinated biphenyl is useful as a heat treating medium and is, in fact, outstanding for such use because many of the disadvantages of oils are overcome yet the desirable aspects thereof are retained. Thus, chlorinated biphenyl provides fire resistance as well as increased oxidative, hydrolytic and thermal stability resulting in uniformity in heat treating operations over long periods of time. When used for quenching the quenching rate of chlorinated biphenyl is approximately the same as oil. For example, chlorinated biphenyl containing 48% combined chlorine required 35.5 seconds to accomplish the same amount of cooling as oil did in about 25 seconds under the same conditions. Accordingly, no significant loss in hardness, as compared to oil quenching, is suffered by quenching in chlorinated biphenyl. Because of these highly desirable characteristics, particularly thermal and oxidative stability and fire-resistance, the process of this invention is also useful for marquenching as well as more conventional, lower temperature, quenching.

The heat treating process of this invention includes quenching by immersing a metal article in chlorinated biphenyl for a length of time sufficient to obtain the results desired, which time will be dependent on considerations such as the section size of said article, its composition, the depth of hardening desired, extent of increase in tensile strength desired, extent of microstructure alteration desired, and the like. Furthermore, a quenching operation can be altered, by controlling the temperature of the chlorinated biphenyl, to the extent of incorporating a quenching and a tempering step in one operation.

Still another operation within the scope of the present invention is to quench by spraying chlorinated biphenyl onto the hot metal instead of using the immersing process heretofore mentioned. This embodiment is particularly important where selective hardening is necessary. In such applications, water cannot be used because there is a likelihood of cracking, and oil is out of the question because of the fire hazard.

It is to be strictly understood that when chlorinated biphenyl is employed as a heat treating medium the operation may be carried on with or without various other types of treatments previous to or subsequent to the heat treatment with chlorinated biphenyl. Examples of other treatments which could be incorporated with the latter operation are: annealing, normalizing, tempering, stress relieving, carburizing, regenerative quenching, marquenching, martempering, heating for homogenization, hot-working, cold-working, sintering, casting, surface treatments, joining, dispersion-hardening and other like treatments.

Here it should also be mentioned that glass, like steel, may be heat treated, that is, tempered, to improve its physical properties, and it is, therefore, contemplated herein that chlorinated biphenyl be used as the heat treating media for tempering glass.

Chlorinated biphenyl containing from about 20% to about 60% by weight of combined chlorine is generally useful in the process of this invention, however, chlorinated biphenyl containing from about 40% to 50% by weight of combined chlorine is preferred as providing heat treating media having viscosity characteristics most suitable for use at usual heat treating temperatures. Chlorinated biphenyl is commercially available as products containing about 21%, 32%, 42%, 48%, 54% and 60% of combined chlorine corresponding approximately to mono-, di-, tri-, tetra-, penta- and hexachlorobiphenyl, respectively. The expressions "chlorinated biphenol containing about 40% to about 50% of combined chlorine" and "chlorinated biphenyl containing about 20% to about 60% of combined chlorine" are used herein as not only including these chlorinated products, but also as blends of one or more of the chlorinated biphenyls whereby the total chlorine content is broadly within the range of 20% to 60%, preferably within the range of 40% to 50% by weight. For example, chlorinated biphenyl containing a total of 45% by weight of combined chlorine can be effectively prepared, for the purpose of this invention, by blending together 50 parts by weight of chlorinated biphenyl containing 42% by weight of combined chlorine and 50 parts by weight of chlorinated biphenyl containing 48% by weight of combined chlorine. In a similar manner, chlorinated biphenyl containing a total of 58% by weight of combined chlorine, for purposes of this invention, may be effectively prepared by blending together 25 parts by weight of chlorinated biphenyl containing 52% by weight of combined chlorine and 75 parts by weight of chlorinated biphenyl containing 60% by weight of combined chlorine. Therefore, for purposes of this invention, chlorinated biphenyl containing generally about 20% to about 60%, or preferably about 40% to about 50%, by weight of combined chlorine may be obtained either by direct chlorination of the biphenyl to obtain the desired combined chlorine content, or a satisfactory material may be obtained by blending together two or more chlorinated biphenyls to obtain a resulting blend of chlorinated biphenyl containing an effective quantity of combined chlorine within the ranges designated above.

The general physical properties of chlorinated biphenyl having varying amounts of combined chlorine are given below.

Property	Percent Chlorine					
	21	32	42	48	54	60
Density:						
Specific Gravity, 25°/25° C. (77°/77° F.)	1.18	1.26	1.38	1.45	1.54	1.62
Pounds per Gallon, 25° C. (77° F.)	9.85	10.55	11.50	12.04	12.82	13.50
Initial Boiling Point, 760 mm. Hg., ° F	527	554	617	644	689	725
Pour Point, ASTM D-97, ° F	34	−32	2	19.4	50	88
Flash Point, Cleveland Open Cup, ° F	286-302	305-310	348-356	379-384	None	None
Fire Point, Cleveland Open Cup, ° F	349	395	None	None	None	None
Viscosity:						
Saybolt Universal 210° F	30-31	31-32	34-35	36-37	44-48	72 78
Sec (ASTM-D-88):						
130° F	35-37	39-41	49-58	69-78	260-340	3,200-4,500
100° F	40-42	47-50	80-93	185-240	1,800-2,500	

None indicates—"no fire point up to boiling temperature."

From the above table of properties, it is seen that chlorinated biphenyl has a very high boiling point, that is, is almost completely fire resistant when there is sufficient chlorine and that the viscosities of chlorinated biphenyl offer wide latitude for various applications and operating temperatures in the practice of the present invention. It is also evident that as the percent of combined chlorine increases there is likewise an increase in boiling point and in viscosity. Such properties support the use of blends of chlorinated biphenyl when faster cooling rates are desired, e.g., in the quenching of steels.

It is known to those skilled in the art that a quenching operation consists of three stages:

(1) In the first stage, or vapor blanket stage, the temperature of the metal is so high that the quenching media is vaporized at the surface of the metal and a thin stable vapor film surrounds the part. The vapor envelope acts as an insulator, and cooling takes place principally by radiation through the vapor film. Cooling speed is relatively slow through this stage.

(2) The second stage, or vapor boiling stage, begins when the metal has cooled to such a temperature that the vapor film is no longer stable. The quenching media then tends to wet the surface of the metal, and violent boiling ensues. Heat is removed from the metal at a very rapid rate as latent heat of vaporization. Cooling is most rapid in this stage.

(3) The third stage, or contact stage, begins when the surface temperature of the metal is reduced to the boiling point or range of the quenching liquid. Below this, boiling ceases and slow cooling takes place by conduction or convection. The rate of cooling is slowest in the third stage.

By making a blend consisting of chlorinated biphenyl having a low boiling point and chlorinated biphenyl having a high boiling point in proportions of about 5:1 to about 25:1, respectively, a quenching medium is obtained which has rates of cooling higher than those obtained by the use of a single chlorinated biphenyl. As the high boiling compound there can also be used chlorinated terphenyl, quatraphenyl or other polyphenyls. This increase in the cooling rate is due to the fact that at the first stage, or vapor blanket stage, the chlorinated biphenyl having a low boiling point has begun to boil while the chlorinated biphenyl possessing a higher boiling point has not. This causes a turbulence or mixing which pierces the vapor film formed about the hot metal, shortening the first stage, or vapor blanket stage. Thus, the second stage, or vapor boiling stage, begins earlier and it is at this stage that cooling is most rapid.

As an illustration of the process of the invention, as well as for comparison with present practices, samples of two commercial grades of steel, a medium and a high carbon steel, were quenched in two different chlorinated diphenyls (one containing about 21% chlorine and the other about 48% chlorine) and in oil. The steels used analyzed as follows.

	Percent
Medium carbon steel:	
C	0.40
Mn	1.00
Mo	1.00
S	0.08
High carbon steel:	
C	0.95/1.05
Cr	0.25
Mn	0.30/0.50
Ni	0.25
P	0.035
Si	0.25/0.50
S	0.035

QUENCHING PROCEDURE

Test 1

Three 1 inch long by ½ inch diameter samples of each grade of steel were austenitized in a Hevi-duty muffle furnace at 1550° F. for one hour. Each sample of the medium and high carbon steel was then quenched in each of the three fluids. The volume of quenching fluid to volume of steel was approximately 400 to 1.

Test 2

Three 2 inch by 3 inch diameter samples of each grade of steel were austenitized in a Hevi-duty muffle furnace at 1650° F. for two hours. Each sample of the medium and high carbon steel was then quenched in each of the three fluids. The volume of oil to steel was approximately 2 to 1.

RESULTS

Test 1.—Hardness tests

The following results were obtained for the average hardness of the medium and high carbon steels quenched according to the present invention in the various fluids.

Quenching fluid:	Average hardness, R_C scale
Chlorinated biphenyl (48% chlorine)	48
Chlorinated biphenyl (21% chlorine)	49
Petroleum oil	53
Quenching fluid:	**Average hardness, R_C scale**
Chlorinated biphenyl (48% chlorine)	45
Chlorinated biphenyl (21% chlorine)	45.5
Petroleum oil	46

Test 1.—Microstructure

The microstructure of both the medium and high carbon steels confirmed the results of the hardness tests.

The microstructure of the samples of high carbon steel quenched in chlorinated biphenyl was somewhat different than that of the high carbon steel quenched in petroleum oil. This difference was also indicated in the hardness results of Table 1. The microstructures of all samples were similar, martensite plus bainite; however, the steel quenched in the petroleum oil contained larger amounts of martensite.

The microstructure of the samples of medium carbon steel, as indicated by the same hardness readings for each of the samples in the three quenching fluids, was identical and independent of the fluid used for quenching. The structure was typically bainitic plus minor amounts of martensite.

Test 2.—Flash point tests

Under the most adverse conditions (volume of quenchant to steel of 2:1), the chlorinated biphenyl fluids neither flashed or fired although boiling resulted. The conventional quenching oil flashed and burned in about 15 seconds after quenching, and the resultant fire was quenched with carbon dioxide.

Microscopic examination of the edges of both the medium and high carbon steels quenched in the two chlorinated biphenyl fluids did not reveal any pitting, decarbonization, or chemical attack by the fluids. In all instances the surface structure was comparable with that of the steels quenched in the conventional petroleum oil.

The hardness results and microstructures of the high carbon steels indicate that chlorinated biphenyl has a somewhat slower cooling rate than the petroleum quenching oil used. This difference in cooling rate is, of course, not evident with the medium carbon steels, because transformation to fine pearlite, bainite, and martensite begins at a much higher temperature for the medium carbon steel than for the high carbon steel, and hence is not as sensitive to the cooling rate.

Chlorinated biphenyl, as described above, comprises the major proportion of the heat treating medium of this invention, and it is generally preferred because of fire prevention considerations that chlorinated biphenyl constitute at least 50%–75% and even more desirable essentially all of such medium. However, it is contemplated that within the scope of this invention the heat treating medium will comprise a homogeneous phase composed of blends of chlorinated biphenyl and oil or

other materials. An example of the physical properties of typical oil-chlorinated biphenyl blends are given in the table below. The oil had the following properties:

API gravity	22–23
Viscosity, 210° F., SUS	160
Flash point, ° F.	545

PHYSICAL PROPERTIES OF OIL-CHLORINATED BIPHENYL BLENDS

Percent by wt.		Specific Gravity	Pounds/gal.
Chlorinated Biphenyl, 48% chlorine	Oil		
50	50	1.1263	9.4
75	25	1.2703	10.6

Additionally, other chlorinated aliphatic and aromatic hydrocarbons such as trichlorobenzene, chlorinated terphenyl and chlorinated naphthalene can be blended with chlorinated biphenyl to provide the heat treating medium used in the process of this invention. In particular, the use of trichlorobenzene in an amount up to about 10% to 15% of the chlorinated biphenyl content is quite desirable where the heat treating operation is to be used under conditions of low temperature, since the viscosity at low temperatures of the resulting blend are significantly reduced by such use of trichlorobenzene without also effecting a significant undesired decrease in the other properties of the chlorinated biphenyl.

It is also contemplated that the chlorinated biphenyl can contain various functional additives such as quenching speed modifiers, viscosity modifiers, wetting agents, antioxidants, rust inhibitors, pour point depressants, and the like, including fatty acids, amines, silica sols, high molecular weight ethylene or propylene oxide polymers, soluble gums, such as carboxy methyl cellulose, methyl cellulose and hydroxy ethyl cellulose, terpene polymer resins, heat treated vegetable oil, residues from petroleum refining, partially oxidized petroleum hydrocarbons, alkylphenolethylene oxide condensates, alkylphenol polyethylene glycols, sodium alkyl sulfates, polyoxyethylene esters of tall oil, organic sulfonates, e.g., sodium sulfonate, barium and calcium sulfonate, metal naphthenates, reaction products of organic sulfonates and a phosphorus sulfide, reaction products of a phosphorus sulfide and an organic amine, mono-, di- and triethanolamine, sodium potassium or ammonium borate, dimers of linoleic acid and other fatty acids, the reaction products of an alkenylsuccinic anhydride, aliphatic acid and polyalkylene polyamine, phosphites, and phenyl-alpha-naphthylamine.

While this invention has been described with respect to various specific examples and embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the heat treating of a material selected from glass and a metal to change the physical characteristics thereof the step comprising heating said material to a temperature below its melting temperature and thereafter cooling said material by contacting with a medium comprising chlorinated biphenyl.

2. In a process for the heat treating of a metal to change the physical characteristics thereof the step comprising heating a metal to a temperature below its melting temperature and thereafter quenching said metal in a medium comprising chlorinated biphenyl.

3. In the process as set forth in claim 2 in which the quenching medium comprises a mixture of a major amount of chlorinated biphenyl and a minor amount of trichlorobenzene.

4. In the process as set forth in claim 2 in which the quenching medium comprises blends of clorinated biphenyl.

5. In the process as set forth in claim 2 in which the quenching medium comprises a mixture of a major amount of chlorinated biphenyl and a minor amount of oil.

6. In a process for the heat treating of steel to change the physical characteristics thereof the step comprising heating steel to a temperature below its melting temperature and thereafter quenching said steel in a medium comprising chlorinated biphenyl.

7. The process of quenching steel which comprises heating steel to a temperature above its transformation range and quenching the heated steel in a quenching medium comprising chlorinated biphenyl.

8. The process of annealing a metal which comprises heating said metal to a temperature at which deformed grains recrystallize to produce new grains and then cooling the recrystallized metal by contacting with a heat treating medium comprising chlorinated biphenyl.

9. The process of precipitation hardening which comprises heating a nonferrous alloy until the phase which precipitates at lower temperatures dissolves and then cooling said alloy by contacting with a heat treating medium comprising chlorinated biphenyl at a rate sufficient to prevent precipitation of said phase.

10. In a process for the heat treating of a metal to change the physical characteristics thereof the step comprising contacting said metal with chlorinated biphenyl which has been heated to a temperature above that of the metal.

11. In a process for the heat treating of a metal to change the physical characteristics thereof the step comprising immersing said metal in a medium comprising chlorinated biphenyl and then heating the metal and chlorinated biphenyl to a temperature above their initial temperature.

12. In a process for the heat treating of glass to change the physical characteristics thereof the step comprising heating glass to a temperature below its melting temperature and thereafter contacting said glass with a medium comprising chlorinated biphenyl.

13. In a process for the heat treating of a metal to change the physical characteristics thereof the step comprising heating a metal to a temperature below its melting temperature and thereafter cooling said metal by contacting with a medium comprising chlorinated biphenyl.

14. In a process for the heat treating of a metal to change the physical characteristics thereof the step comprising heating a metal to a temperature below its melting temperature and thereafter cooling said metal by contacting with a medium comprising a major amount of chlorinated biphenyl and a minor amount of chlorinated terphenyl.

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