Aug. 19, 1958 G. L. FLEMMERT ET AL 2,848,362

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

Filed March 11, 1957 8 Sheets-Sheet 1

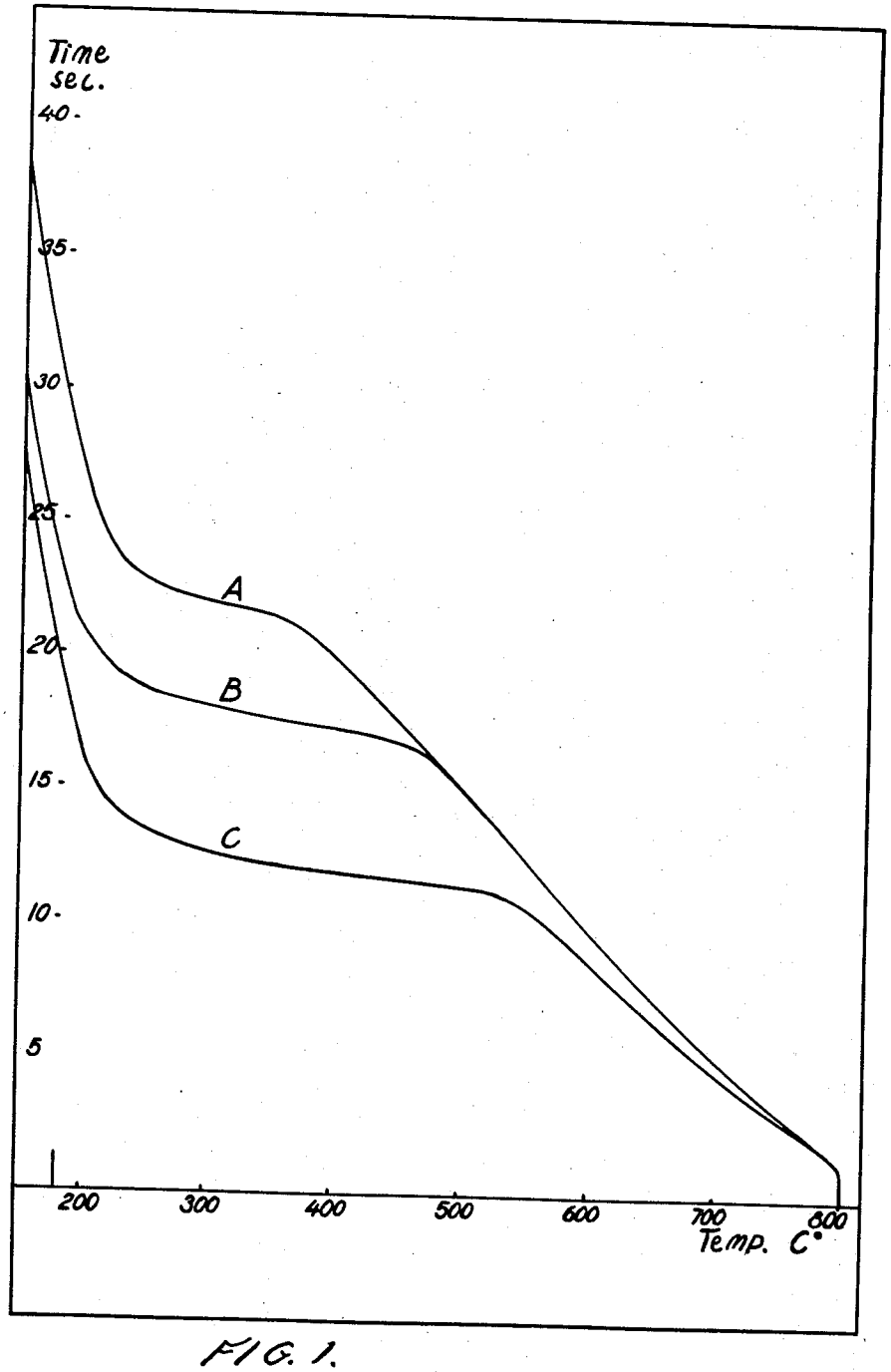


FIG. 1.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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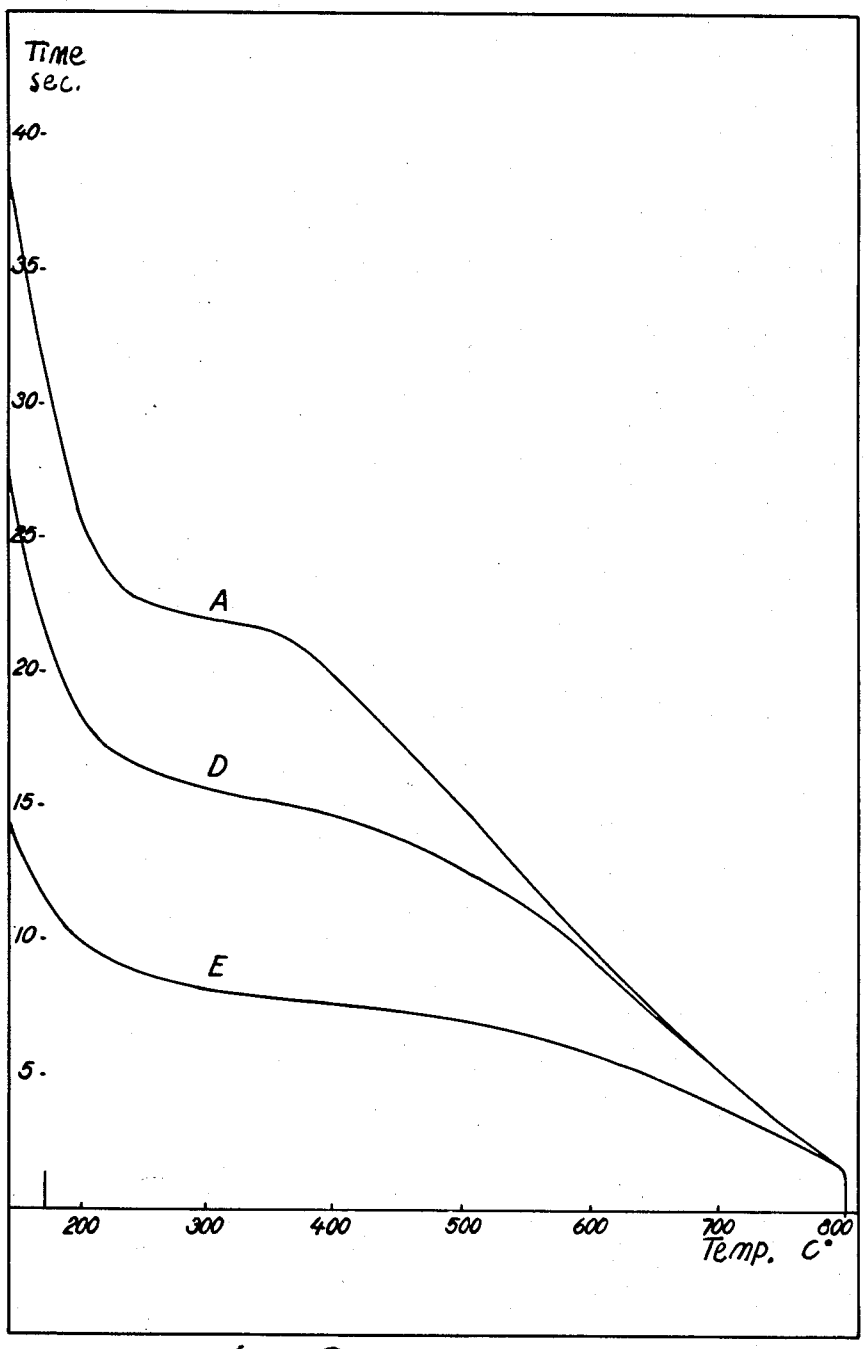


FIG. 2.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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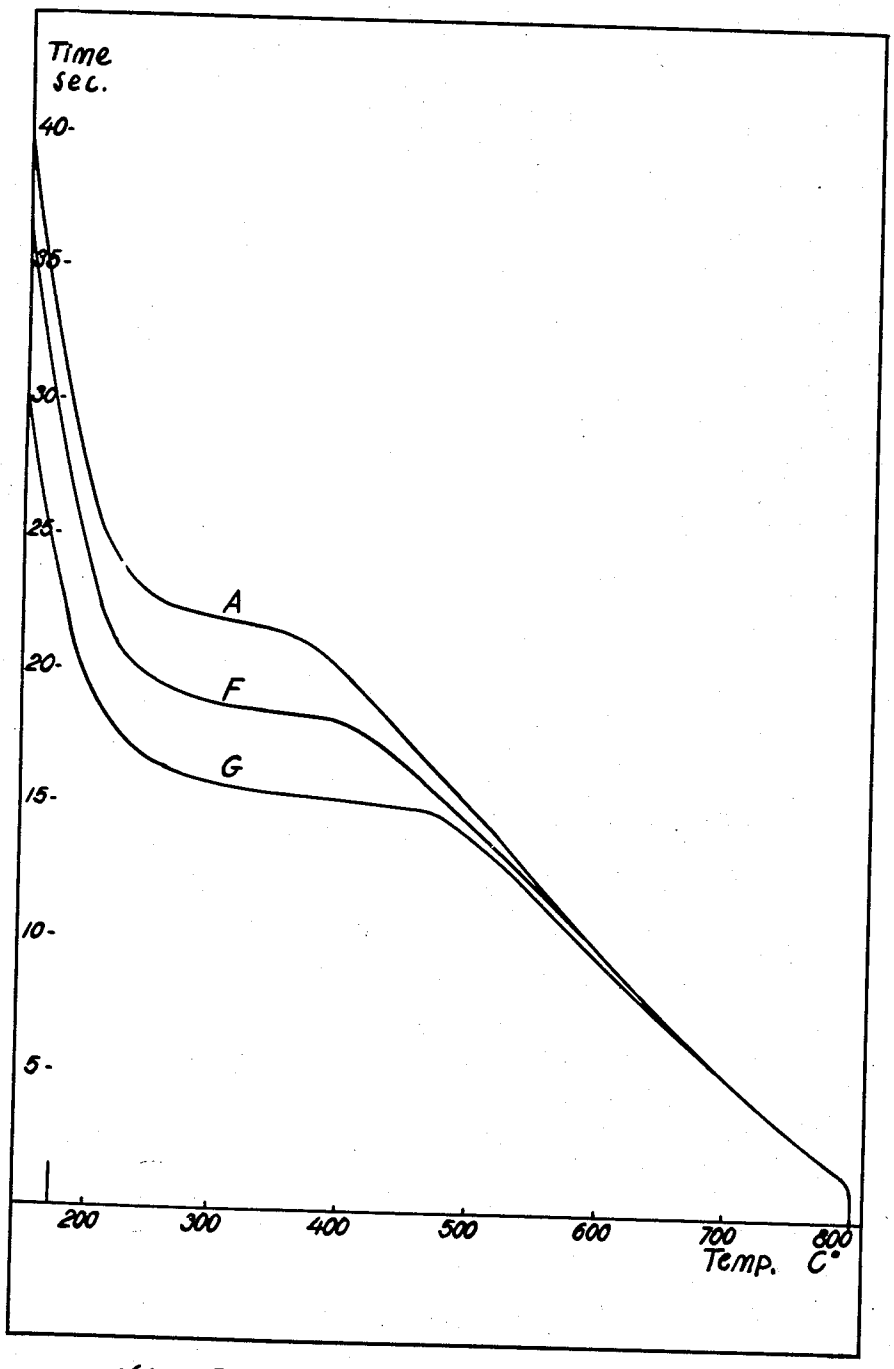


FIG. 3.

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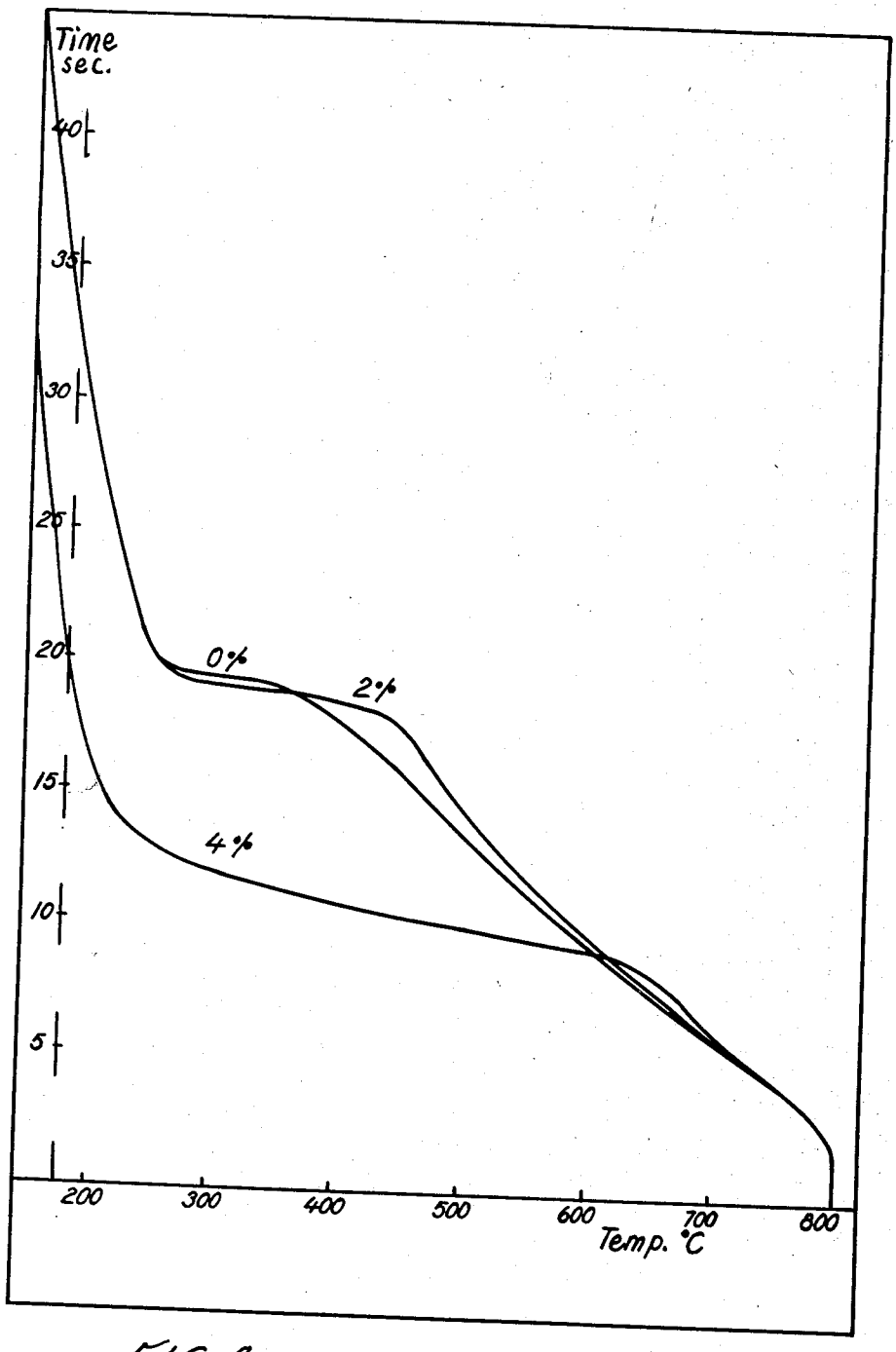


FIG. 4.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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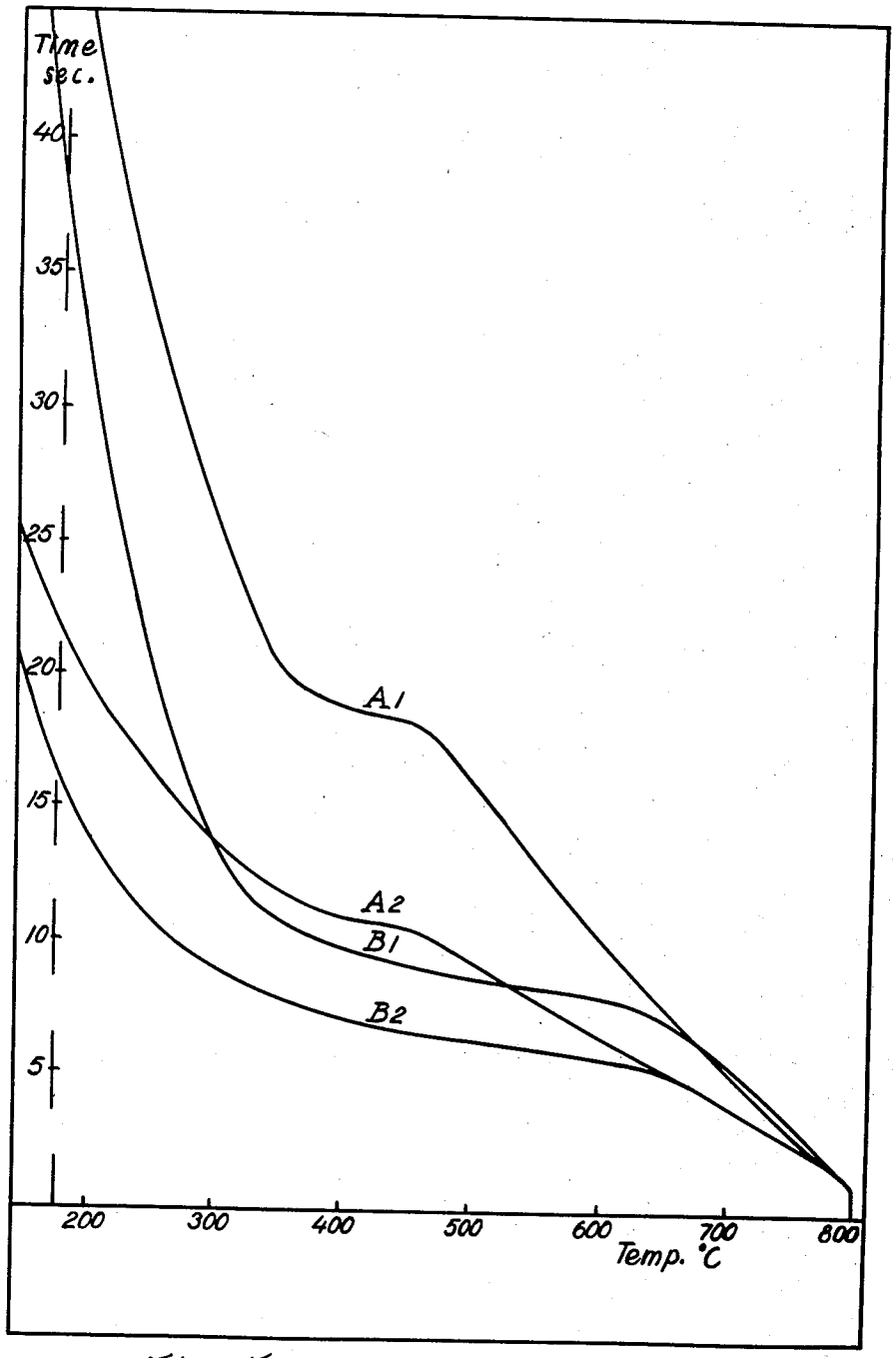


FIG. 5.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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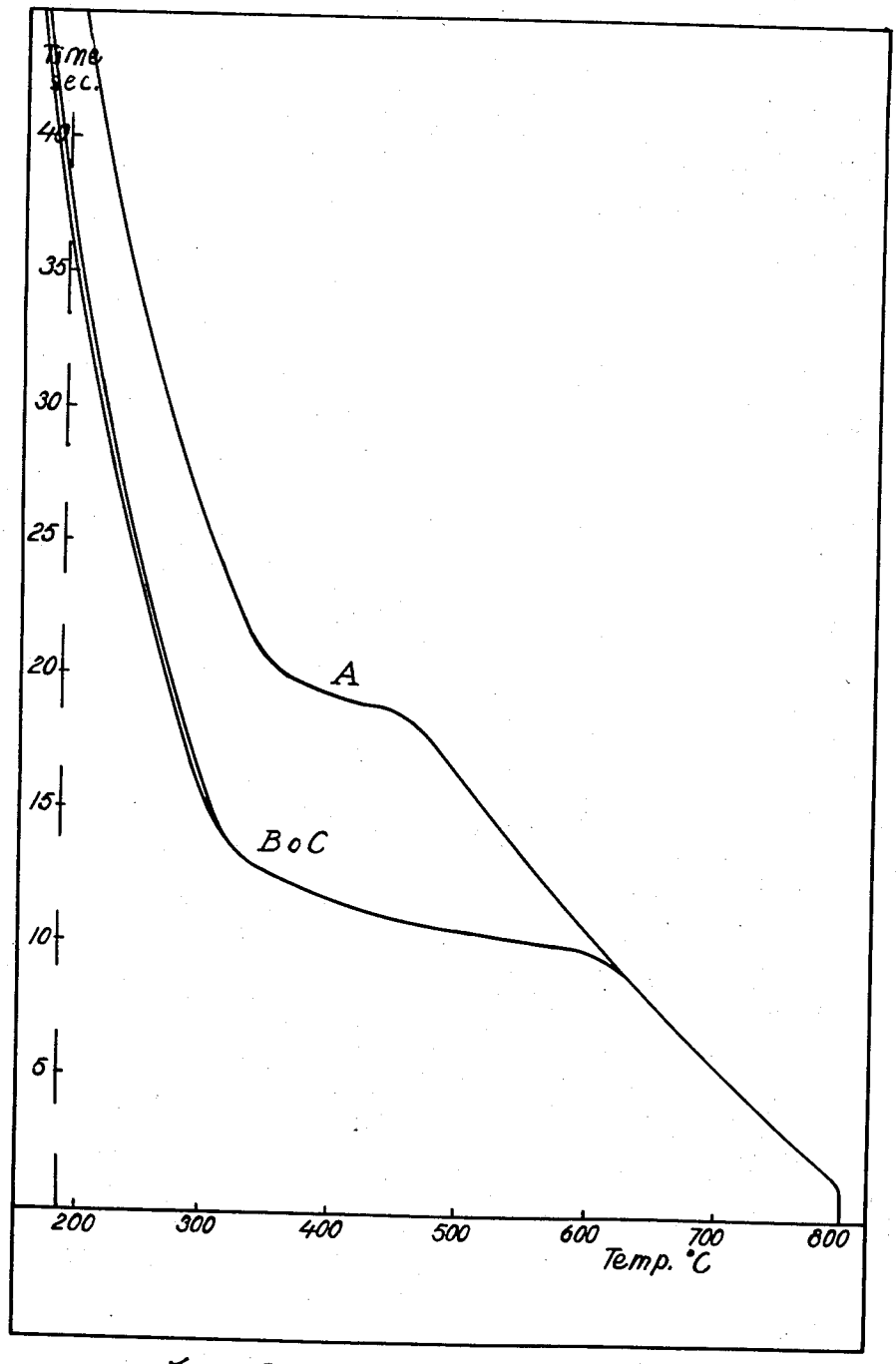


FIG. 6.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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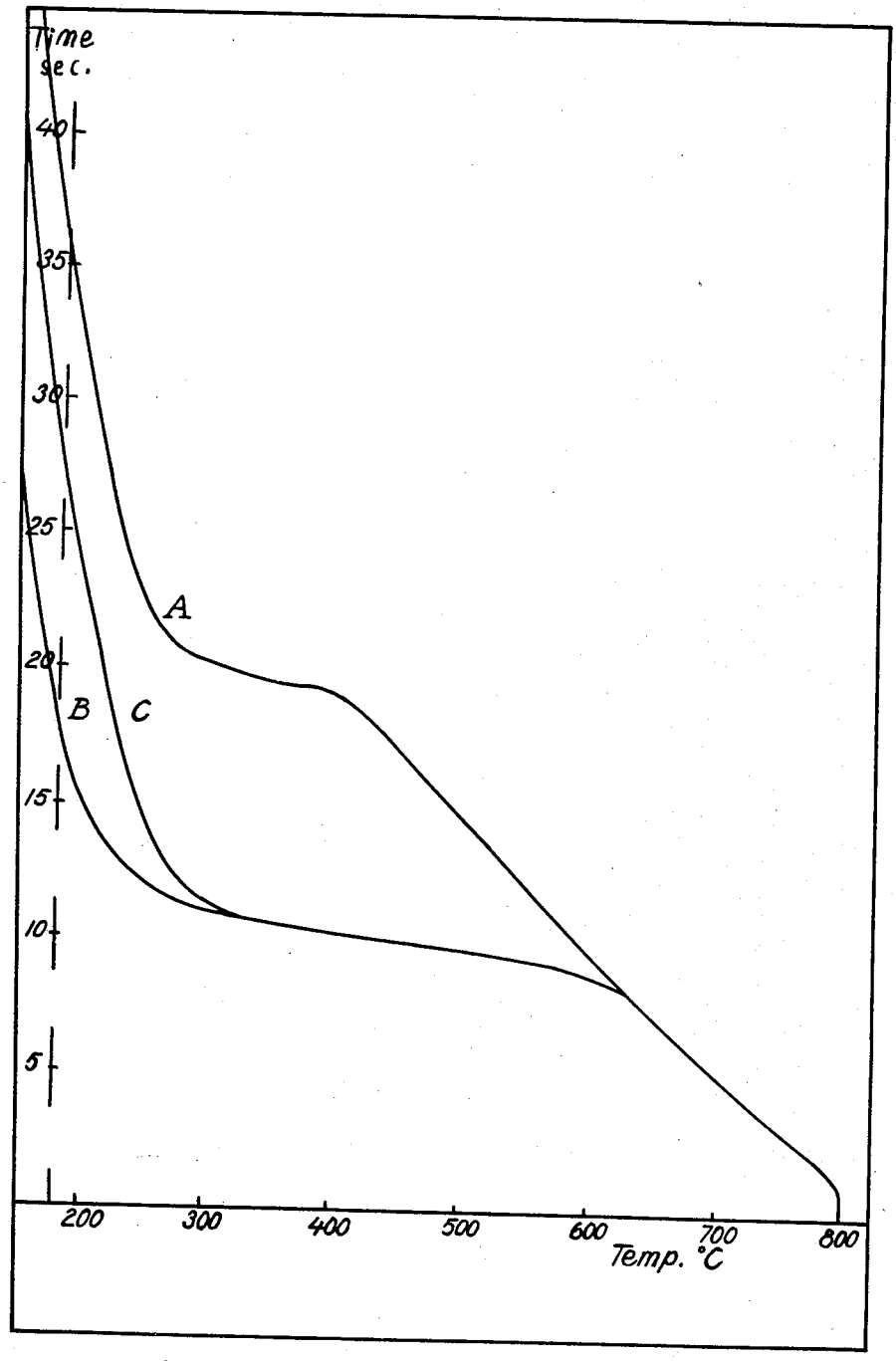


FIG. 7.

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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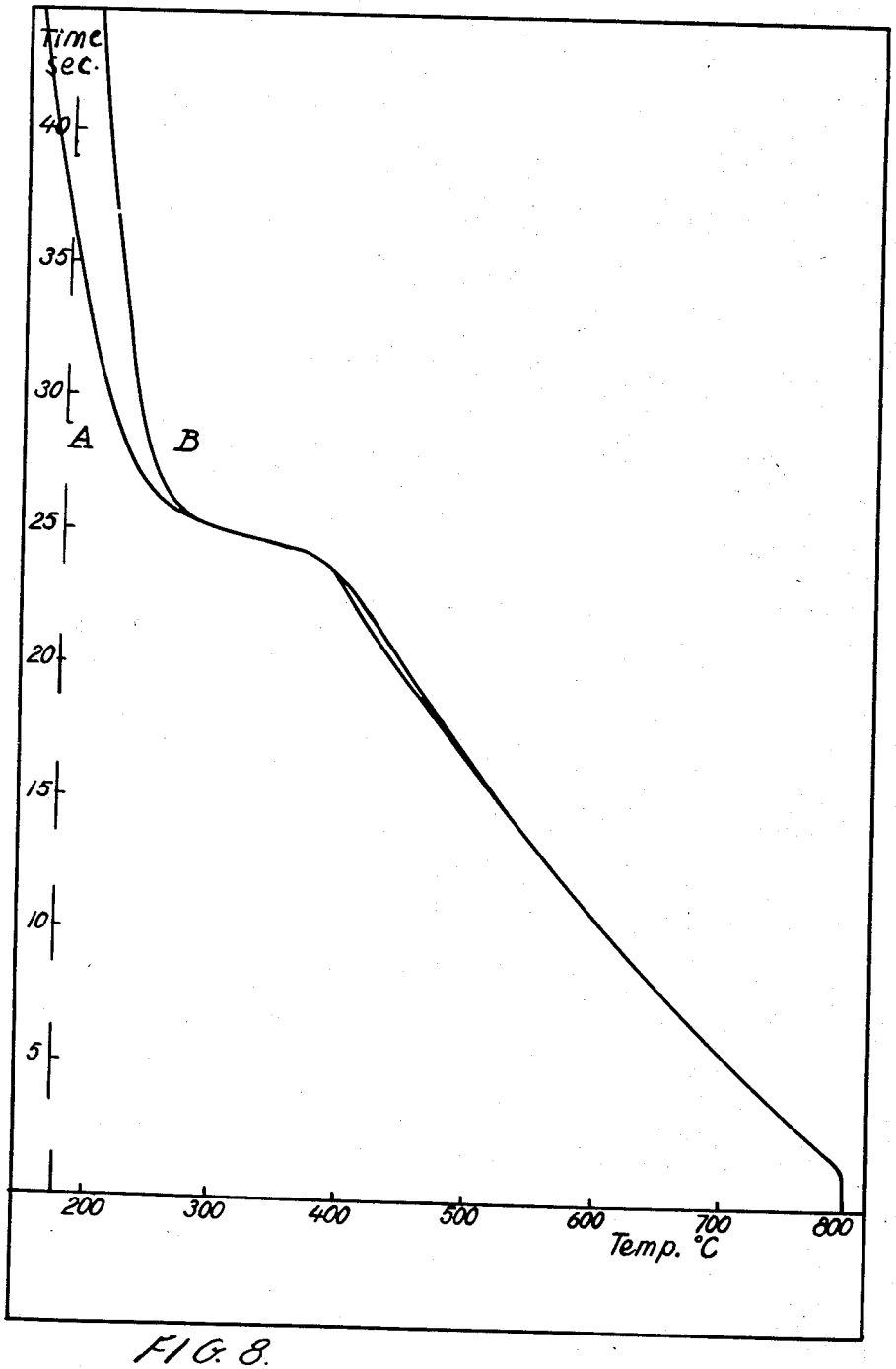


FIG. 8.

United States Patent Office 2,848,362
Patented Aug. 19, 1958

2,848,362

METHOD OF QUENCHING METAL ARTICLES IN A MINERAL OIL

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Application March 11, 1957, Serial No. 645,340

Claims priority, application Sweden March 10, 1956

10 Claims. (Cl. 148—13.1)

The present invention relates to a process for cooling metal articles, particularly articles of steel and steel alloys. More particularly the invention relates to a process for quenching metal articles with the aim of effecting a hardening of the metal surface of said articles. The invention is not limited to treatment of steel articles, even if it is products of this metal that are particularly contemplated in the present case, but includes also treatment of articles of other metals such as silver, copper, aluminium and alloys of these metals, which are to be subjected to rapid cooling from a high temperature, such as in the range of 250–1100° C.

For hardening of steel articles, such as balls, shafts, razor blades, springs, axes and other tools, said articles are heated to a temperature at which they are incandescent, that is, to a temperature in the range of 600–1000° C. for instance 800° C. Due to this heating an intercrystalline conversion of the ferrite of the steel into austenite is effected. If the steel is slowly cooled, the austenite is converted into the so-called pearlite (or sorbite or sorbitic pearlite, a mixture of ferrite and cementite, Fe_3C) but on rapid cooling there is instead formed martensite, particularly in the surface layer, which modification results in the steel having a harder surface. As a certain depth from the surface of the metal article treated (how far from the surface depends on the efficiency of the hardening) there is a somewhat softer transition zone, consisting of so-called troostite, i. e. a mixture of martensite and sorbite or sorbitic pearlite. It is thus evident that it is of great importance to be able to effect a rapid cooling, at least at the temperatures at which the aforesaid conversions occur. The critical temperature is considered to be about 550° C.

For cooling metal articles, water or oil has been used, particularly oil of mineral origin. Of these agents water results in the most rapid cooling but when the temperature drops below 300° C., cracks are easily formed in the material if the subsequent cooling is rapid. Below 300° C. oil thus provided the most suitable cooling rate, but against this, the cooling within the critical temperature range according to the above-mentioned definition, viz. between about 550° C. and 300° C., will generally be too slow, which will result in a diminished formation of martensite, and accordingly a lower hardness of the steel article such as steel articles of the aforesaid definition.

During the cooling of a metal article in a liquid three different stages can be observed. If primarily a ball has been heated for example up to 800° C. and is at this temperature rapidly immersed into a liquid having a temperature for example within the range of −60° up to +100° C., near to the surface of the ball there is formed a layer of vapour, which will make the heat transfer difficult at the higher temperatures. After a certain cooling has occurred, the liquid gets into closer contact with the hot ball, which results in that so-called bubble or point boiling occurs. This stage (hereinafter

called the second stage) is characterized by a very good heat transfer. In the last stage the boiling has ceased and the heat transfer, which will at this time be smaller, occurs by convection and conduction of heat.

As mentioned above, oil has been used hitherto as cooling agent in cooling metals, for instance in quenching to effect hardening. By the expression "oil" is meant products, which as base component contain hydrocarbons of various molecular weights, boiling point ranges and different structures, such as paraffinic, olefinic, naphthenic or aromatic hydrocarbons or mixture thereof. Particularly, hydrocarbon fractions having a boiling point exceeding 150° C. are used as hydrocarbons, such as lube oil distillates, gas oil and kerosene.

It has been previously suggested to use in hardening of steel articles a mineral oil having as an additive certain hydrocarbon sulphonic acid salts, viz. salts of a sulphonic acid, in which the sulphur is directly combined with a hydrocarbon radical. It is stated that in quenching steel articles the above-mentioned second stage is more rapidly reached by chilling in oil, if the oil has this additive. The disadvantage with the said sulphonic acid salts containing hydrocarbon radicals within the surface active range, viz. having more than 6 carbon atoms in the molecule, lies in that said sulphonic acid salts are easily decomposed at the prevailing high temperature, which results in that corrosive cracking products, primarily SO_2, are formed. In certain cases these corrosive cracking products have appeared to be able to affect the articles to be hardened in a disadvantageous manner. It has furthermore appeared that in order to reach a satisfactory thermal stability of hardening oils having hydrocarbon sulphonic acid salts as an additive, the oils need also to have stabilizing additives, such as certain special derivates of phosphoric sulphides, for example those disclosed in the United States Patent 2,536,403.

It has now been found that the aforesaid disadvantages are obviated and the above-mentioned second cooling stage is reached at a considerably higher temperature, that is in a shorter time period, and thus a surprisingly rapid cooling is obtained, if as cooling agents oils are used, to which have been added a salt or salts of a carboxylic acid in which at least one carboxylic acid group is combined with a cyclic hydrocarbon group or a hydrocarbon group in which there is included at least one cyclic group. The hydrocarbon group should contain more than 6 carbon atoms, and preferably more than 10 to 12 carbon atoms, and may be exclusively cyclic, as for example in abietic acid or naphthoic acid, or mixed aromatic-aliphatic, such as in alkylaryl carboxylic acids, for instance naphthalene acetic acid or phenyl-butyric acid, and alkylaryl carboxylic acid, for instance veratric acid or mixed naphthenic-aliphatic, as in naphthen-alkyl carboxylic acids, for instance trimethyl-cyclopentyl-valeric acid or chaulmoogric acid, and alkylnaphthene carboxylic acid, for instance butyl-cyclopentane monocarboxylic acid or sedanonic acid. Particularly suitable for use according to the present invention are salts of the carboxylic acids occurring in mineral oil fractions from naphthenic base oils boiling within higher temperature ranges and which by a common name are called naphthenic acids. Such acids contain a cyclic saturated ring, that is a naphthenic ring, usually a 5-ring in the hydrocarbon radical, and this ring is preferably combined with an alkyl group. The metals which may be combined with the carboxylic acid radical are primarily those of group 2 of the periodic system, that is the alkaline earth metals, particularly magnesium, calcium and barium, as well as zinc and cadmium, and those of group 4:b of the periodic system, particularly tin and lead, together with the metals of the iron group of the

periodic system, particularly iron itself. The metal ions are preferably not more than in the bivalent stage. Salts of tri- or higher-valent metals result in many cases in an undesirable thickening of the oil and salts of monovalent metals are usually too strongly hygroscopic and do therefore not show satisfactory solution properties.

The usefulness of the aforesaid additives according to the present invention are thus based on the fact that they result in a new effect in the cooling, which cannot be predicted when starting from the present state of the art. Contributory reasons to this usefulness are the relatively good thermostability of the cyclic compounds and the particular property of the decomposition products of the carboxylic acid salts, that they do not cause any corrosion or undesirable deposits. This applies particularly to the exclusively cyclic compounds, viz. the salts of abietic acid which do not form any corrosive decomposition products, since if any decomposition occurs they are decomposed into carbon dioxide and water. Due to the solubility of the additives the result is attained that there is no risk that the active molecules be present at insufficient concentration near to the metal article to be cooled.

Additives not forming solutions with oils or which are present in the same in suspended condition yield, when mixed with said oils, temperature-sensitive cooling baths, in which precipitates may be easily formed. Low solubility of the additives may also result in gels being formed in the oil bath.

Suitable amounts of the additives according to the invention are up to about 5%, based on the weight of cooling agent. Higher amounts of additives, such as up to about 10%, may however be used, but it has appeared that the effect of the additive will be constant at amounts exceeding about 5%. The above stated percentages relate of course to the amount of active additive, which may, if desired, be added in mixture with inert components, such as hydrocarbon oil. Thus, if suitable in the production of the additive, a concentrate of the active additive in the base oil to be used in the final quenching oil may be prepared. From this it thus follows that it is usually uneconomic to use a greater amount of additive than that corresponding to the value of about 5%. The minimal amount of additives to the oil is at about 0.2%. However, the contents should exceed about 0.5%, preferably about 1%.

In the present invention a mineral oil is preferably used, as cooling agent, that is an oil, which consists of hydrocarbons to the essential part. Such an oil may be refined, for example by means of sulphuric acid or by solvent extraction, deparaffination, de-asphaltation and the like. Oils containing cyclic hydrocarbons, for instance obtained from naphthenic base oils, are in many cases particularly usable in the process according to the invention, on one hand due to their better solvent properties regarding a number of these additives and on the other hand due to their good thermal stability.

It has appeared to be particularly suitable, especially from an economic point of view, to use as additives in the oils of the process according to the invention calcium naphthenate in the form as obtained in vacuum distillation of naphthenic acid-containing mineral oils in the presence of CaO or $Ca(OH)_2$, lime or other alkaline agents.

In addition to the effect that corrosion is prevented by cooling with cooling agents having additives according to the invention, the inventors found in certain cases a corrosion-inhibiting effect on the articles treated. This applies particularly for zinc naphthenate.

Furthermore it has appeared to be suitable to use as a metallic component of the additive for the cooling agent according to the invention the same metal as that intended to be subjected to rapid cooling from a high temperature, particularly when it is desired to prevent the metal in question becoming contaminated. Particularly this applies to articles of iron and steel, which may preferably be hardened in quenching oils added with carboxylic acid salts of iron, in which at least one carboxylic acid group is combined with a cyclic hydrocarbon radical. By adding to the quenching oil also metal inhibiting agents, comprising for example organic phosphites, such as triphenyl phosphite, the catalytic oxidizing effect of the iron in the iron naphthenate is counteracted, when said salt is used according to the invention.

It is advantageous to use oil having in addition to the stated additives, other types of antioxidants, such as methyl-di-isobutyl phenol and phenyl-α-naphthyl amine, and/or anticorrosives, such as esters and ethers of dibasic acids and complex amines.

In order to characterize an oil to be used as quenching agent, one may use the temperature, at which the cooling process passes from the first to the second (more rapid) stage. This temperature is called the "characteristic temperature" of the quenching oil. By a special method, which will be described hereinafter, it has been possible to show in an illustrating way, how this characteristic temperature is altered in a favourable direction by adding substances according to the present invention.

A silver ball, the central temperature of which is measured by a thermo-element combined with a registering instrument, is heated in an electric furnace to the desired temperature, viz. in the examples stated to 800° C. Then the ball is rapidly immersed in the cooling oil, the cooling process being indicated by a time-temperature diagram obtained at the same time. The reason for selecting silver as metal in this investigation is on one hand that silver has a very good heat conductivity and on the other hand that the surface of the silver is not so easily destroyed after repeated investigations. Both these properties assist in obtaining reproduceable results.

To investigate the durability of the effect produced by the additives according to the present invention a hardening apparatus was constructed, the upper part of which consisted of a tube furnace. This furnace was arranged a little inclined and was fed with steel balls at its upper end, which were allowed to roll through a zone heated to 900–1000° C. When discharged at the lower end of the furnace the balls were immediately allowed to fall down into a bath of cooling oil maintained at a temperature below 50° C. After being cooled the immersed balls were lifted up from the bath and the oil was allowed to be drained from the balls back into the bath. By weighing the balls a relatively large definite weight of balls could in this way be hardened in a small quantity of oil, and a measure of the stability of oil, calculated on kgs. hardened balls per kg. oil, could be obtained. The cooling property of the oil was then tested by the method with silver ball stated above.

Example 1

The silver ball is cooled in the way described above in a light petroleum lube oil (without additives, Figure 1A), the viscosity and vapour pressure of which are so chosen that the passage from the second to the last cooling stage occurs at a suitable temperature. The cooling curve obtained is as shown at Figure 1A. Then 20 and 40 gms. per litre respectively of a calcium naphthenate-containing product are added to samples of the oil. When the oil with this additive is used for cooling according to the aforesaid, a more rapid cooling process is obtained, which is illustrated by Figure 1, B and C. The curve B shows the result in the presence of 20 gms. per litre of the aforesaid product, which in turn contains about 5% by weight calcium. The calcium percentage of the cooling oil will thus be about 0.1% by weight. The curve C shows the result, when said Ca-percentage is 0.2% by weight, i. e. the total of additives is 40 gm. per litre or about 4% by weight.

Example 2

The same experiment was repeated with the addition of two different amounts of zinc naphthenate, 2.55 and 5.1% by weight, respectively. Then the curves D and E, respectively, of Figure 2 were obtained. As a comparison the curve obtained without additives A was also plotted.

The zinc naphthenate of this example contained 7.8% by weight Zn and the amounts of zinc in the oils used for the cooling was 0.2 (D) and 0.4 (E)% by weight respectively. Here, it should be observed that the cooling in the vapour film stage is already more rapid when using these additives in the oil.

Example 3

The same experiment was repeated, but with addition of two different amounts of lead naphthenate: 1.9 and 4.8% by weight, respectively. Then the curves F and G, respectively, of Figure 3 are obtained. Curve A shows the result without any additive.

The lead naphthenate of this example contained 21% by weight Pb and the amount of lead in the oils used for the cooling was 0.4 (F) and 1.0 (G)% by weight, respectively. It is evident that a more rapid cooling is obtained (in the presence of salts of this metal), which is primarily reached due to an increase of the so-called characteristic temperature, defined previously.

Example 4

The same experiment was repeated, but now with addition of different amounts, 2 and 4% by weight, respectively, of a product containing about 90% calcium abietate. Then the curves of Figure 4 are obtained disclosing that in the first case the characteristic temperature is increased from about 350° C. to 420–440° C., and in the second case to considerably over 550° C.

Example 5

The cooling rate may be improved by agitation of the hardening bath (curve A1 without and curve A2 with agitation, Figure 5) but a larger improvement is obtained by the additives used in the present invention. In fact the improvement is so good, in the use of, for example, 3.3% by weight calcium abietate (curve B1 without and curve B2 with agitation, Figure 5), that no further significant increase of the characteristic temperature can be obtained by agitation. The agitation speed was 6 litres oil per minute (in the silver ball apparatus as described above).

Example 6

The stability of the hardening oil, that is the durability of the effect obtained by the additives according to the invention, is shown in Figure 7, in which A illustrates the cooling process of a transformer oil fraction without any additives, B the cooling process of unused oil of the same kind, with 3.3% by weight calcium abietate added, and C the cooling process of the last-mentioned oil after use for hardening steel balls in the hardening apparatus as described provided with a tube furnace. 530 kgs. of steel balls had been hardened per kg. oil present in the hardening bath at the start. During this hardening the losses of oil obtained gradually were made up by 1.92 kg. oil of the same kind (and having the same additive dissolved therein, viz. 3.3% by weight calcium abietate). The oil according to curve C was thus used for hardening on the average 530/2.92=181 kgs. steel balls per kg. oil.

Example 7

An oil similar with that used in Example 6, also now with 3.3% by weight calcium abietate, was used on an industrial scale. The hardening bath contained 20,000 litres of oil. In this bath 200 tons steel casting were hardened. Samples of the quenching oil were taken out after hardening of 47 and 122 tons, and the cooling effect was tested with the silver ball according to the method described. The results are disclosed on Figure 6, B and C. The same curve was also obtained with the freshly prepared quenching oil and curve A shows the result with the same oil prior to the addition of the calcium abietate. As no fresh oil was added to the bath, about 10 kgs. castings per kg. oil were hardened without any alteration of the oil. The hardening result on the steel products was very good.

Example 8

Using transformer oil with a carboxylic acid salt, not of cyclic structure added, the cooling effect was tested as above with silver ball. The result is shown on Figure 8, curve A without additive and curve B with about 2% by weight sodium stearate. On a comparison with for example the results in Figures 1–4 the advantages of the additives used in the invention are obvious insofar as with the sodium stearate used as additive no displacement of the characteristic temperature was obtained.

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

1. A method of quenching metal articles comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 0.2–10% of a metallic salt of a cyclic carboxylic acid.

2. A method as claimed in claim 1, in which the oil has incorporated therein a bivalent metallic salt of a cyclic carboxylic acid.

3. A method of quenching articles of a metal selected from the group, which consists of steel and steel alloys, comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 0.2–10% of a bivalent metallic salt of a cyclic carboxylic acid.

4. A method as claimed in claim 3, in which the oil has incorporated therein 1–5% of a bivalent metallic salt of a cyclic carboxylic acid.

5. A method of quenching articles of a metal selected from the group, which consists of steel and steel alloys, comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 0.2–10% of a bivalent metallic salt of a naftenic acid.

6. A method of quenching articles of a metal selected from the group, which consists of steel and steel alloys, comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 0.2–10% of a bivalent metallic salt of abietic acid.

7. A method of quenching articles of a metal selected from the group, which consists of steel and steel alloys, comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 1–5% of a bivalent metallic salt of a naftenic acid.

8. A method of quenching articles of a metal selected from the group, which consists of steel and steel alloys, comprising heating said articles to a temperature at which said articles are incandescent, immersing said heated articles in a bath of a mineral oil, the components of which have a boiling point of at least 150° C. and have incorporated therein 1–5% of a bivalent metallic salt of abietic acid.

9. A method as claimed in claim 7 comprising using a calcium salt of naftenic acid.

10. A method as claimed in claim 8 comprising using a calcium salt of abietic acid.

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