Patented Feb. 1, 1944

2,340,724

UNITED STATES PATENT OFFICE

2,340,724

QUENCHING OF METALS

Clifford G. zur Horst, Hampton Township, Allegheny County, Blaine B. Wescott, Churchill Borough, and Leslie W. Vollmer, Pittsburgh, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

No Drawing. Original application January 12, 1942, Serial No. 426,536. Divided and this application July 13, 1943, Serial No. 494,530

4 Claims. (Cl. 148—13.1)

This invention relates to the quenching of metals; and it is particularly concerned with improved quenching oil compositions comprising a light mineral quenching oil and an oil-soluble, heat-stable, high molecular weight iso-olefin polymerization product in a controlled amount adequate to produce a quenching oil composition having an initial five second quenching speed of at least about 22.0 per cent without substantially modifying the stress-reducing characteristics of the oil; and it further comprises an improved method of quenching metals wherein the preheated metal is quenched by immersion in a quenching oil bath consisting essentially of a mineral quenching oil and a controlled amount of an oil-soluble, heat-stable, high molecular weight iso-olefin polymerization product adequate to impart to said bath an initial five second quenching speed of at least about 22.0 per cent without substantially modifying the stress-reducing characteristics of the oil; all as more fully hereinafter set forth and as claimed.

While our invention is useful in the quenching of any metal which is advantageously quenched in an oil bath having a high initial quenching speed, it is particularly useful in the quenching of iron base alloys and it will be described hereinafter in detail in connection with the quenching of steel.

Many metal alloys, particularly iron base alloys, such as carbon steels and alloy steels, require heat treatment for the development of maximum properties of hardness and strength. These properties are dependent upon the establishment of certain physical structures in the metallic components of the alloy. In steel, hardenability is determined by the extent to which a martensitic structure is established in the alloy. The production of this structure in steel is usually accomplished by arresting at the desired point, the changes in the internal structure of the alloy which take place during the cooling of the steel from high temperatures. The fact that these physical changes require time for their completion makes it possible to arrest them at the desired point by suitable quick cooling.

Quenching of the steel in aqueous or oil quenching baths is generally used to arrest these physical changes. It is advantageously carried out in such manner that the physical changes in the steel are arrested at or near the point at which maximum hardness is obtained, and is then followed by a tempering treatment involving heating at relatively low temperatures to impart the desired ductility or toughness to the metal at some sacrifice in hardness.

Quenching in aqueous quenching media develops the properties of strength and hardness to the maximum obtainable for a given section of metal. However, quenching in aqueous quenching media is undesirable in many cases because these media tend to set up excessive amounts of internal stress in the steel resulting in distortion and warping and, in the extreme case, cracking of the quenched piece. As a result, aqueous quenching media have been supplanted by mineral oil quenching media where such mineral oil quenching media have sufficiently high quenching speeds to produce the desired properties in the quenched metal because such mineral oil quenching media are particularly adapted to minimize internal stresses and distortion in the quenched product. This results from the fact that the quenching speeds of mineral oil quenching media are substantially slower than those of aqueous quenching media, due to considerable extent to the formation of a more or less persistent vapor envelop about the quenched piece at the beginning of the quenching cycle, and the fact that in the later stages of the quenching cycle the quenching speeds of mineral oil quenching media are sufficiently slow so that the internal stresses developed in the metal in the early stages of the cycle tend to be relieved. However, since the overall cooling efficiency of the mineral oil quenching media heretofore known is not as great as that of aqueous quenching media, it has been difficult or impossible to effect in mineral oil quenching baths quenching of pieces formed of steels having high critical cooling rates, sufficiently rapidly to develop the properties of strength and hardness to their maximum values, or the quenching of pieces having high mass to surface ratios, sufficiently rapidly to develop the properties of hardness and strength to the maximum depth.

It is desirable therefore to improve the quenching of metals in mineral oil quenching media so that the cooling efficiency in the early stages of the quenching cycle is increased to more nearly approach the cooling efficiency of aqueous quenching media without increasing the quenching speed in the later stages of the cycle sufficiently to deleteriously affect the normal stress-relieving properties of the mineral oil.

It is an object achieved by the present invention to provide a method of quenching metals, particularly iron base alloys, in mineral quenching media having quenching speeds greater than

the mineral oil quenching media heretofore known. It is a further object achieved by the present invention to provide mineral quenching oil compositions having cooling efficiencies more nearly approaching the cooling efficiency of water while retaining the stress-preventing characteristics of oil quenches.

The critical cooling rate of a metal is defined as the lowest cooling rate at which maximum hardness is developed. For steel the critical cooling rate is the lowest cooling rate which will produce a full martensitic structure in the steel. Thus it is generally most desirable to effect initial quenching at a speed sufficient to produce a cooling rate at least equal to the critical cooling rate for as great a depth in the metal as possible and to effect the quenching with a minimum of distortion.

The cooling efficiency of a quenching medium is customarily defined in terms of quenching speed and the initial five second quenching speed is a convenient measure of this property of quenching oil compositions, and is the property with which this invention is most concerned. The initial five second quenching speed of a quenching oil composition as referred to throughout this specification and in the appended claims is determined according to the following formula:

$$\frac{\text{Temperature rise in 5 sec. test}}{\text{Temperature rise in cold quench test}} \times 100 = \text{Per cent available heat removed in first five seconds}$$

in which the respective values are measured as follows:

Cylindrical test pieces one inch in diameter and 2.5 inches long of stainless steel containing about 18.0 per cent of chromium and 8.0 per cent nickel are heated for one hour at 1500° F. in a furnace equipped with an automatic temperature control. Two quarts of the quenching oil composition to be tested are placed in a calorimeter which has a wire screen positioned in the center of the oil bath to insure constant depth of immersion of the samples. The quenching composition is heated to an initial temperature of 100° F.

One of the preheated test pieces is immersed in the quenching bath by means of light tongs for a period of five seconds without agitation. The test piece is then removed and the bath agitated and the maximum temperature reached is measured. A second preheated test piece is immersed in the bath at an initial temperature of 100° F. and the bath is agitated until the maximum rise in temperature has been produced. The maximum temperature rise measured in this cold quench represents the available heat of the test piece. By substituting the values thus determined for the five second quench and for the cold quench in the above formula a measure of the heat removed in the first five seconds as compared with the total available heat is obtained and is referred to herein as the initial five second quenching speed.

We have discovered that certain oil-soluble, heat-stable, high molecular weight iso-olefin polymerization products have the property of increasing the intial five second quenching speed of mineral oils without lessening their stress-reducing characteristics, and that by incorporating such heat-stable, high molecular weight iso-olefin polymerization product in suitable amounts in light mineral oils of the type heretofore used in quenching metals, we can produce quenching media having initial five second quenching speeds of at least 22.0 per cent, while retaining the distortion-minimizing characteristics of mineral oil quenching media. We have found further that by quenching pieces formed of metals having high critical cooling rates or pieces difficult to quench because of a high ratio of mass to surface, by immersion in quenching oil compositions containing these heat-stable, high molecular weight iso-olefin polymerization products, we can effect cooling of the metal at a rate more nearly approaching or equal to the critical cooling rate of the metal without creating excessive stresses in the metal. In this way we have been able to develop the hardness of metals having high critical cooling rates to a degree heretofore unattainable with oil quenching media and have been able to effect hardening to a greater depth in pieces having high ratios of mass to surface, and have achieved both results with a minimum of distortion.

The heat stable, high molecular weight iso-olefin polymerization products which we have found suitable for the purposes of our invention are such as are obtained by the polymerization of iso-olefins such as isobutene in the presence of boron trifluoride, aluminum chloride, active clays or other polymerization catalysts at relatively low temperatures usually below 0° C. The polymerization products obtainable in this way have high molecular weights ranging from 1000 to 150,000. However, for the purposes of our invention, the polymers having molecular weights above about 10,000 are generally not sufficiently heat stable to give satisfactory life to quenching media containing them. Isobutene polymerization products having molecular weights between about 1,000 and about 10,000 are particularly advantageous for the purpose of our invention. These isobutene polymerization products, when used in amounts corresponding to about 0.5 to 6.0 per cent by weight, yield quenching compositions having initial five second quenching speeds between about 22.0 and 30.0 per cent the highest values being obtained in the range of about 1.0 to 3.0 per cent by weight.

These materials have the property, when incorporated in a light mineral oil in suitable amount, of substantially increasing the initial five second quenching speed of the oil without deleteriously affecting its stress-relieving properties. The effect of these materials in increasing the initial quenching speed of the oil is due mainly to a decrease in the persistence of the vapor envelop formed when the hot metal is first immersed in the quenching oil bath. By incorporating them in mineral oils such as have been used heretofore for quenching metals, we have found that quenching oil compositions having initial five second quenching speeds of at least about 22.0 per cent can be produced.

The various heat-stable, high molecular weight iso-olefin polymerization products do not increase the initial five second quenching speed of a mineral oil in the same degree. Some are more effective than others and they can be used in different amounts. We have found also that in most cases the effectiveness of each polymerization product increases directly with the amount added up to a maximum and then decreases and the optimum range for different polymerization products may differ.

In compounding the quenching oil compositions of our invention we select for the quenching bath a mineral oil of the type customarily used for quenching steel and other metals. The oils used for this purpose may be either naphthenic

or paraffinic oils and are usually acid treated neutral oils having a viscosity of about 70 to 200 S. U. V. at 100° F., relatively high flash and fire points, and substantial heat stability and resistance to sludging. For optimum results we have found that paraffinic oils which usually have an initial five second quenching speed between about 17.0 and about 19.0 per cent are most advantageous.

The best results are obtained according to our invention by incorporating in the oil an amount of heat-stable, high molecular weight iso-olefin polymerization product sufficient to produce a quenching oil composition having an initial five second quenching speed which can effect cooling of the metal to be quenched at a rate approaching the rate obtainable with aqueous quenching media. In the case of many steels, initial five second quenching speeds of at least about 22.0 per cent are required for this purpose, and particularly for the quenching of many pieces having high mass to surface ratios these high initial five second quenching speeds are particularly advantageous.

We have found also that mixtures of the heat-stable, high molecular weight iso-olefin polymerization products may be used according to our invention. However, in such case, the effect of the respective polymers may not be entirely additive and the optimum amounts of the respective polymers, when used alone, may produce less satisfactory results in mixtures than do somewhat smaller amounts of each polymer.

The actual quenching operation using the quenching compositions of our invention is usually carried out by immersion of the preheated metal in the quenching oil composition until sufficient heat has been removed to reduce its temperature the desired amount. The quenching oil may be used repeatedly with only slight deterioration.

In the following example there is illustrated specifically the results obtainable with several concentrations of a heat-stable, high molecular weight iso-olefin polymerization product used in accordance with the process of our invention.

A series of quenching oil compositions was made up using a neutral paraffinic mineral oil having a viscosity of 100 S. U. V. at 100° F. and concentration of a heat-stable, high molecular weight iso-olefin polymerization product between 1 and 5 per cent. The particular polymer used had a molecular weight of about 7000. The initial five second quenching speeds of the respective compositions were then determined as above described and the following results were obtained:

	Quenching speed
Quenching oil No. 2	16.98
Quenching oil No. 2+1.0% polymer	29.46
Quenching oil No. 2+2.0% polymer	29.83
Quenching oil No. 2+3.0% polymer	30.23
Quenching oil No. 2+4.0% polymer	28.81
Quenching oil No. 2+5.0% polymer	27.06

It will be observed from the results of this test that the optimum concentration of this particular polymer was about 3 per cent and that all concentrations between 1 and 5 per cent produced quenching oil compositions having initial five second quenching speeds substantially above 22.0%.

This application is a division of our copending parent application Serial No. 426,536, filed January 12, 1942.

While we have described our invention with reference to certain specific embodiments thereof, it is to be understood that it is not limited to such specific embodiments except as hereinafter defined in the appended claims.

What we claim is:

1. An improved quenching oil composition comprising a mineral quenching oil and a heat-stable, high molecular weight iso-olefin polymerization product in controlled amount adequate to impart to said quenching oil composition an initial five second quenching speed of at least about 22.0 per cent without substantially modifying the stress-reducing characteristics of the oil.

2. An improved quenching oil composition comprising a light mineral quenching oil and 0.5 to 6.0 per cent by weight of a heat-stable, high molecular weight iso-butene polymerization product.

3. A method of quenching metals comprising heating the metal to a temperature above its critical temperature and thereafter cooling the metal by immersion in a quenching oil bath comprising a light mineral oil and a controlled amount of a heat-stable, high molecular weight iso-olefin polymerization product adequate to impart to the quenching oil bath an initial five second quenching speed of at least about 22.0 per cent.

4. A method of quenching metals comprising heating the metal to a temperature above its critical temperature and thereafter cooling the metal by immersion in a quenching oil bath comprising a light mineral oil and 0.5 to 6.0 per cent by weight of a heat-stable, high molecular weight iso-olefin polymerization product.

CLIFFORD G. zur HORST.
BLAINE B. WESCOTT.
LESLIE W. VOLLMER.