Patented Oct. 4, 1949

2,483,725

UNITED STATES PATENT OFFICE

2,483,725

HIGH-SPEED QUENCHING

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No Drawing. Application October 26, 1946, Serial No. 706,076

4 Claims. (Cl. 148—13)

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This invention relates to an improved process of quenching metals and, more particularly, is directed to an improved method of quenching metals wherein the heated metal is quenched by immersion in a quenching oil bath comprising a mineral oil and a mixture of partially oxidized hydrocarbons derived from petroleum, shale oil or like mineral hydrocarbonaceous starting materials such as tar oils, derived from the low temperature coking of coal, lignite, and the like.

It has been found, in accordance with the present invention, that a minor proportion of certain partially oxidized petroleum hydrocarbon products, hereinafter described in detail, when incorporated in a mineral oil quenching bath substantially increases the quenching speed of said bath without substantially modifying the stress-reducing characteristics of the oil.

This invention is applicable in the quenching of any metal which is advantageously quenched in an oil bath having a higher initial quenching speed but it is particularly useful in the quenching of metal alloys, particularly ferrous alloys and carbon steels. Such alloys and steels require heat treatment for the development of increased hardness and strength. The hardness and strength of a given alloy is dependent largely upon certain physical structure. In the case of steel, the hardness is determined by the proportion of martensite obtainable in the alloy. To increase the hardness of the metal alloys, they are heated to a high temperature and then the metal at red heat is plunged into a comparatively cool quenching bath. Frequently the alloys are quenched to obtain maximum hardness and are then tempered to the desired hardness and ductility.

Usually the quenching bath consists of a mineral oil. Water or aqueous solutions as quenching media produce maximum hardness for a given section of metal because they quench the hot metal at a much higher rate than ordinary mineral oil. However, the use of aqueous quenching baths results in setting up excessive internal stresses in the metal alloy, causing distortion, warping and, in some cases, cracking. Mineral oils as quenching media have the valuable property of cooling the alloy slowly after it has been reduced to about 600° F. to 700° F. They have the added advantage of maintaining a substantially uniform quenching speed over a wide range in temperature variation of the quenching bath itself. These valuable properties tend to minimize internal stresses and distortion in the metal alloy.

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The disadvantage of ordinary mineral oils as quenching media is that they do not offer the desirable high initial quenching rates that are characteristic of aqueous baths. This disadvantage is particularly important in the manufacture of certain steels having high critical cooling rates. Ordinary mineral oils when used as quenching baths for such steels do not offer initial quenching speeds sufficiently high to effect maximum steel hardness. From the above it will be apparent that the development of quenching media offering initial quenching speeds approaching that of water, and retaining the hereinabove mentioned valuable characteristics of a mineral oil media, is a development of considerable importance.

It is an object of this invention to provide a mineral oil quenching composition having a high initial quenching speed. Another object is the provision of an improved method for quick quenching metals in a mineral oil bath without substantially modifying the stress-reducing characteristics of the oil. A further object is the provision of a means of substantially increasing the initial 5-second quenching speed of a mineral oil quenching bath without substantially modifying the stress-reducing characteristics of the oil. These and other objects of this invention will become apparent from the following description.

This invention is predicated on the discovery that mineral oils having incorporated therein a minor proportion of substantially neutral, partially oxidized petroleum hydrocarbons have all the advantages of ordinary mineral oils as quenching media and, in addition, exhibit initial quenching speeds far surpassing those of ordinary mineral oils. It has thus been discovered that small amounts of a particular partial oxidation product of petroleum hydrocarbons, when added to a mineral oil, give rise to a quenching composition characterized by a high initial quenching speed.

The partial oxidation product employed in quenching oil baths, in accordance with this invention, is a mixture of materials produced by the liquid-phase controlled partial oxidation of a mixture of petroleum hydrocarbons, such as ceresin wax, paraffin wax, rod wax, scale wax, amorphous wax and higher boiling petroleum distillates, or mixtures of two or more of the above, the oxidation being effected by blowing air of other oxygen-containing gas through a liquid body of the petroleum hydrocarbon mixture maintained at a temperature above at least 100° C. and not greater than about 185° C. and at a pressure greater than atmospheric pressure but not substantially above about 350 pounds per square inch. Since the partial oxidation product employed in the present invention is derived from compounds which are soluble in petroleum hydrocarbons but insoluble in water and since the yield of said petroleum-soluble compounds may be substantially reduced by protracted oxidation, by the conversion of a portion thereof to petroleum-insoluble acidic compounds, it is preferred not to extend the oxidation treatment beyond the point of incipient formation of the above described petroleum-insoluble compounds. Incipient formation of petroleum-insoluble compounds in the reaction mixture may be noted by simple observation of a test sample taken from the mixture or by titration of such a sample.

The resulting reaction product is a mixture of a great number of different compounds which may be grouped as follows:

1. Unoxidized (original) hydrocarbons
2. Aliphatic alcohols, largely secondary and tertiary
3. Aliphatic ketones
4. Keto-alcohols
5. High molecular weight saturated aliphatic carboxylic and hydroxycarboxylic acids
6. Neutral esters and lactones derived from the aforesaid acids and the aforesaid alcohols or from the aforesaid acids, respectively.

The above compounds are all of relatively high molecular weight, that is, they consist of aliphatic chains of more than 5 carbon atoms each and extend up to chain lengths of about 35 carbon atoms. Differently grouped, the mixtures are separable broadly into saponifiables and unsaponifiables. Into the latter group fall the alcoholic and ketonic compounds and the unoxidized hydrocarbons, whereas the acids, esters and lactones are grouped as saponifiables. For use in the present invention, as an additive to a quenching oil composition, one or more of the neutral, unsaponifiable types of oxidized products, that is, the alcoholic, ketonic, and/or keto-alcoholic compounds, are selected. It has been found preferable to employ in the present relation the unsaponifiable partial oxidation products obtained from ceresin or from higher melting point petrolatums. Particularly advantageous for increasing the quenching speed of a mineral oil are the unsaponifiable, substantially neutral bodies separated from the reaction product obtained by oxidizing, in the above described manner, a mixture of crude scale white wax and petrolatum.

A substantially effective separation between the unsaponifiables and the saponifiables of the aforesaid partial oxidation reaction mixture may be effected by treating the mixture with a hot aqueous solution of a caustic alkali to saponify, as completely as possible, all the saponifiable compounds contained therein. Unsaponifiable components of the reaction mixture collect by gravity separation as a supernatant oily layer above a subnatant layer of the saponified components. The two layers are then resolved by decantation or other separation means and the product derived from the unsaponifiable component layer, consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids, is employed in the quenching oil composition of this invention.

The above described mixture of unsaponifiable, substantially neutral bodies separated from the reaction product obtained in accordance with the aforesaid partial oxidation treatment is, in general, characterized by an acid number of 0.0 to 5.0, a saponification number of 15 to 45 and a maximum iodine number of 40. The general physical properties of the mixture are as follows:

Specific gravity @158° F	.842–.898
Viscosity (Saybolt) @ 210° F secs	48–58
Melting point (Ubbelohde) °F	100–107
Flash point °F	350–370
Fire point °F	420–440

It is quite common to compare quenching media by reference to their initial quenching speed as measured by the initial 5-second quench rating as determined according to the following formula:

$$\frac{\text{Temperature rise in 5-second test}}{\text{Temperature rise in complete quench test}}\times 100=\frac{\text{Per cent available heat removed}}{\text{(in first 5 seconds)}}$$

The values used in the above calculation are determined as follows: A stainless steel sphere of definite weight (200 grams) is heated in an electric furnace equipped with automatic control for 20 minutes at a temperature of 1500° F. Fifteen hundred grams of the oil to be tested are placed in a calorimeter equipped with an agitator which revolves at a definite speed.

The heated sphere is immersed in the quenching bath adjusted to 90° F. for a period of five seconds with agitation at a definite speed. The sphere is then removed and the bath agitated, and the maximum temperature reached is measured. A second test is made in which the heated steel sphere at 1500° F. is immersed in the bath at an initial temperature of 90° F., and the bath is agitated until a maximum rise in bath temperature has been produced. The maximum temperature rise measured in this complete quench test represents the available heat of the steel sphere. By substituting the value thus determined for the five-second quench and for the complete 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. The following table gives the comparison of initial quenching rates, determined in the above manner, for ordinary paraffin base mineral oil having a viscosity (S. U. V.) of 70 seconds at 100° F. and the same oil having added thereto varying proportions of the unsaponifiable, substantially neutral oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said unsaponifiables being characterized by the chemical and physical properties set forth above.

Quenching Media	Initial 5-Second Quenching Speed (Percentage of Total Temperature Rise)
Mineral oil	22.7
98% Mineral oil, 2% Neutral bodies from petroleum wax	34.0
95% Mineral oil, 5% Neutral bodies from petroleum wax	40.8
90% Mineral oil, 10% Neutral bodies from petroleum wax	42.8
85% Mineral oil, 15% Neutral bodies from petroleum wax	42.9
80% Mineral oil, 20% Neutral bodies from petroleum wax	42.5

From the above table it will be noted that the addition of a minor proportion of the neutral partial oxidation product derived from petroleum wax and consisting essentially of a mixture of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids substantially increases the initial 5-second quenching speed of the oil. The optimum percentage of said partial oxidation product that should be added to a given conventional mineral oil will depend largely on the characteristics of the mineral oil involved but generally will be between about 2 and about 30 per cent by weight of the quenching composition. The mineral oil used in the above described quenching compositions may be any of the distillate oils having a boiling range of from about 450° F. to about 900° F., a flash point above about 300° F. and a viscosity (S. U. V.) within the range of from about 50 to about 150 seconds at 100° F. The oils employed may be paraffinic, naphthenic, mixed base oils, and the like. It will thus be understood that this invention contemplates broadly a mineral oil quenching composition having incorporated therein minor proportions of the above described partially oxidized petroleum hydrocarbon products and the method of quick quenching metals by immersion thereof in baths comprising said compositions.

We claim:

1. A method of quenching heated metals which comprises immersing the heated metal in a mineral oil bath containing a minor amount sufficient to substantially beneficially affect the initial 5-second quenching speed of said oil, of a mixture of neutral, substantially unsaponifiable oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said mixture of neutral, substantially unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids.

2. A method of quenching heated metals which comprises immersing the heated metal in a mineral oil bath containing a minor amount sufficient to substantially increase the initial 5-second quenching speed of said oil, of a mixture of neutral, substantially unsaponifiable oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said mixture of neutral, substantially unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids.

3. A method of quenching heated metals which comprises immersing the heated metal in a mineral oil bath having incorporated therein an amount between about 2 and about 30 per cent by weight of a mixture of neutral, unsaponifiable oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said mixture of neutral, unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids.

4. An improved quenching oil composition containing from about 70 to about 98 per cent by weight of a mineral oil having a boiling point range of from about 450° F. to about 900° F., a flash point above about 300° F. and a viscosity (S. U. V.) within the range of from about 50 to about 150 seconds at 100° F. and from about 2 to about 30 per cent by weight of a mixture of neutral, unsaponifiable oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said mixture of neutral, unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids.

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