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QUENCHING OIL COMPOSITIONS

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This invention relates to improved quenching oil compositions for use in the metallurgical industries and to the methods of quenching metals where such oil compositions are employed.

Many metal alloys, particularly iron base alloy such as carbon steels and other alloy steels, require heat treatment for the development of maximum properties of hardness and strength. These desirable properties are dependent upon the establishment of certain physical structures in the metallic components of the alloy brought about by heat treating such alloys under conditions which will bring about the desired structure. Having obtained the structure which will give maximum hardness and strength to the alloy by the proper heat treatment, the structure formed by such heat treatment can be "trapped" by rapidly cooling the heated alloy before the structure has a chance to change or be modified.

The treatment of cooling the heated metal alloy is known as quenching. The rate of quenching or cooling depends largely upon the type of steel and the finishd properties desired. It is desirable to have as rapid a rate of cooling as possible through the desired temperature range but the rate must not be so rapid as to produce cracks or excessive brittleness.

The quenching of steel has been done in aqueous or oil quenching baths. Although satisfactory properties of strength and hardness in steel can be obtained by quenching in aqueous quenching media, such quenching is undesirable in many cases because the aqueous media tend to set up excessive internal stresses in the iron alloy resulting in distortion and warping, and in some cases even cracking of the pieces being quenched. In an attempt to overcome the undesirable features of aqueous quenching, quenching in mineral oils and in animal or vegetable oils and combinations thereof have been used. Quenching in oleaginous media is not always satisfactory because of the tendency of such media to deteriorate because of the high temperature involved in the quenching operation.

It is an object of the present invention to provide an oleaginous quenching composition which will satisfactorily remove heat from the metal being quenched and which also possesses thermal stability. It is a further object of the invention to provide a mineral oil quenching composition having satisfactory cooling efficiencies and which will not set up excessive internal stresses in the metal being quenched. A further object of the present invention is to provide a method of quenching metals such as steels in mineral oil

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quenching compositions having desirable cooling efficiencies and which is thermally stable under the quenching conditions. Further objects and advantages of the invention will become apparent from the following description thereof.

We have discovered that the above objects can be attained by employing as a quenching medium a composition comprising an oil such as an animal, vegetable or a hydrocarbon oil, preferably a petroleum oil, in which have been incorporated small amounts of a preferentially oil-soluble soluble sulfonate soap, particularly preferentially oil-soluble sulfonates obtained in the treatment of petroleum oils with sulfuric acid, and in combination therewith a small amount of a neutralized reaction product of a phosphorus sulfide and a hydrocarbon, particularly an olefin polymer. The composition should have a total water content of from about 0.01% to about 0.25%, and preferably from about 0.05% to about 0.2%.

The oil used, comprising a major proportion of the composition, can be suitably an oil obtained from Mid-Continent, Pennsylvania, or coastal type crude oils. The oils having a Saybolt Universal viscosity at 100° F. of from about 80 seconds to about 200 seconds, and preferably from about 100 seconds to about 150 seconds are suitable. Because of the high temperatures involved in the quenching operation the oil should have a minimum flash point of about 300° F. Blends of oils of various viscosities can also be used. For example, we can use blends of distillate oils of suitable viscosity, e. g. 80–85 seconds Saybolt Universal viscosity at 100° F., and sufficient filtered stock steam refined oil to give a blended oil of the desired viscosity.

The preferentially oil-soluble sulfonates are employed in the range of from about 0.1% to about 10%, and preferably from about 1% to about 5%, while the neutralized reaction product of the phosphorus sulfide and the hydrocarbon are employed in the range of from about 0.05% to about 5%, and preferably from about 0.25% to about 2%. The percents given herein and in the appended claims are weight percentages.

The neutralized reaction product of the phosphorus sulfide and the hydrocarbon contains as constituents thereof a metal, phosphorus and sulfur. The phosphorus sulfide employed can be, for example, P_2S_3, P_4S_3, P_4S_7, P_4S_{10}, and preferably P_2S_5.

The hydrocarbon constituent of the reaction can be aliphatic, cyclo aliphatic or aromatic, such as for example, paraffins, olefins, olefin polymers, terpenes, benzene, naphthalenes, an-

thracene, etc. Preferably, the hydrocarbon is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or iso-mono-olefinic hydrocarbons such as propylenes, butylenes, and amylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing iso-mono-olefins and mono-olefins of less than 6 carbon atoms. The polymers may be obtained by the polymerization of these olefins or mixtures of olefins in the presence of a catalyst such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and iso-mono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example by the polymerization in the liquid phase of a hydrocarbon mixture containing mono-olefins and iso-mono-olefins such as butylene and isobutylene at a temperature of from about —80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts type such as, for example boron fluoride, aluminum chloride and the like. In the preparation of these polymers we may employ, for example, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline.

A suitable polymer for the reaction with phosphorus sulfide is the product obtained by polymerizing in the liquid phase a hydrocarbon mixture containing butylenes and isobutylenes together with butanes and some C_3 and C_5 hydrocarbons at a temperature between about 0° F. and 30° F. in the presence of aluminum chloride. A suitable method for carrying out the polymerization is to introduce the aluminum chloride into the reactor and introduce the hydrocarbon mixture, cooled to a temperature of about 0° F., into the bottom of the reactor and passing it upwardly through the catalyst layer while regulating the temperature within the reactor so that the polymer product leaving the top of the reactor is at a temperature of about 30° F. After separating the polymer from the catalyst sludge and unreacted hydrocarbons, the polymer is fractionated to obtain a fraction of the desired viscosity, such as for example, from about 80 seconds to about 2000 seconds Saybolt Universal at 210 F.

Another suitable polymer is that obtained by polymerizing in the liquid phase a hydrocarbon mixture comprising substantially C_3 hydrocarbons in the presence of an aluminum chloride complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with isooctane. The temperature in the reactor is controlled within the range of about 50° F. to about 110° F. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upwardly through the catalyst layer. The propane and other saturated gases pass through the catalyst while the propylene is polymerized under these conditions. The molecular weight of the propylene polymer is about 500 to about 1000.

Other suitable polymers can be obtained by polymerizing a hydrocarbon mixture containing about 10% to about 25% isobutylene at a temperature of from about 0° F. to about 100° F., and preferably 0° F. to about 32° F. in the presence of boron fluoride. After the polymerization of the isobutylene, together with a relatively minor amount of the normal olefin present, the reaction mass is neutralized, washed free of acidic substances and the unreacted hydrocarbons subsequently separated from the polymers by distillation. The polymer mixture so obtained, depending upon the temperature of reaction, varies in consistency from a light liquid to viscous, oily material and contains polymers having molecular weights ranging from about 100 to about 2000 or higher. The polymers so obtained may be used as such, or the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights, and suitable fractions obtained reacted with the phosphorus sulfide to obtain the desired reaction products. The bottoms resulting from the fractionation of the polymer which may have Saybolt Universal viscosities at 210° F., ranging from about 50 seconds to about 10,000 seconds, are well suited for the purpose of the present invention.

Essentially paraffinic hydrocarbons such as bright stock residua, lubricating oil distillates, petrolatums, or paraffin waxes may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons, with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride and the like.

Examples of high molecular weight olefinic hydrocarbons which can be employed as reactants are cetene (C_{16}), cerotene (C_{26}), melene (C_{30}) and mixed high molecular weight alkenes obtained by cracking petroleum oils.

Other preferred olefins suitable for the preparation of the herein-described phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms are in a long chain. Such olefins can be obtained by the dehydrogenation of paraffins, such as by the cracking of paraffin waxes or by the dehalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

As a starting material there can be used the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons resulting from the vapor phase cracking of paraffin waxes in the presence of aluminum chloride which is fully described in United States Patents Nos. 1,995,260, 1,970,002, and 2,091,398. Still another type of olefin polymer which may be employed is the polymer resulting from the treatment of vapor phase cracked gasoline and/or gasoline fractions with sulfuric acid or solid absorbents such as fuller's earth, whereby unsaturated polymerized hydrocarbons are removed. Also contemplated within the scope of this invention is the treatment with phosphorus sulfide of the polymers resulting from the voltolization of hydrocarbons as described, for example in United States Patents Nos. 2,197,768 and 2,191,787.

Also contemplated within the scope of the present invention are the reaction products of a phosphorus sulfide with an aromatic hydrocarbon, such as for example benzene, naphthalene, toluene, xylene, diphenyl and the like, or with an alkylated aromatic hydrocarbon such as for example benzene having an alkyl substituent having at least four carbon atoms and preferably at

least eight carbon atoms, such as a long chain paraffin wax.

The phosphorus sulfide-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulfide, for example P_2S_5 with the hydrocarbon at a temperature of from about 200° F. to about 500° F., and preferably from about 200° F. to about 400° F., using from about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere, such as for example an atmosphere of nitrogen above the reaction mixture. Usually it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a solvent such as hexane, filtering and subsequently removing the solvent by suitable means such as by distillation. If desired, the reaction product can be further treated with an agent having an active hydrogen atom, such as steam at an elevated temperature of from about 100° F. to about 600° F.

The phosphorus sulfide-hydrocarbon reaction can be carried out in the presence of sulfur or an organic compound capable of decomposing to form free sulfur, as described and taught in Reissue 22,464.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus-sulfide hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent. Other metal constituents such as a heavy metal constituent can be introduced into the neutralized product by reacting the same with a salt of the desired heavy metal.

The neutralized phosphorus-sulfide-hydrocarbon reaction product can be obtained by treating the reaction product with suitably basic compounds such as hydroxides, carbonates, oxides or sulfides of an alkaline earth metal or an alkali metal, such as for example, potassium hydroxide, sodium hydroxide, sodium sulfide, CaO, etc. Other basic reagents can be used such as for example ammonia or an alkyl or aryl substitute of ammonia such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the reaction product either as such or dissolved in a suitable solvent such as naphtha with a solution of the basic reagent, for example potassium hydroxide or sodium hydroxide dissolved in alcohol. As an alternative method, the reaction product can be treated with solid alkaline compounds such as KOH, NaOH, Na_2CO_3, $KHCO_3$, K_2CO_3, CaO and the like at an elevated temperature of from about 100° F. to about 600° F. As was aforesaid, when the phosphorus sulfide-hydrocarbon reaction product is neutralized with a basic reagent containing a metal constituent, the neutralized reaction product is characterized by the presence of the metal constituent of the basic reagent. Neutralized reaction products containing a heavy metal constituent, such as for example tin, titanium, aluminum, chromium, cobalt, zinc, iron and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with a basic reagent. It will be understood that when the neutralization is accomplished with a polyvalent basic material such as lime, a product having excess basicity may be obtained. Reference is made to U. S. Patents 2,316,080, 2,316,082, and 2,377,955, in which detailed descriptions are given for the preparation of phosphorus sulfide-hydrocarbon reaction products of the foregoing type.

The following examples illustrate methods of preparing the neutralized reaction product of a phosphorus sulfide and a hydrocarbon. These examples are given by way of illustration only and are not intended to limit the scope of the invention.

EXAMPLE I

A mixture of 200 parts of 1000 molecular weight butylene polymer and 44 parts of P_2S_5 are heated and stirred at 400° F. under N_2 for six hours, during which time a total of 4.9 parts sulfur are added in equal dumps at hourly intervals. 119 parts of SAE 10 grade oil are then added and the product neutralized by the slow addition at 400° F. of a solution of 27.7 parts KOH in an equal weight of water. The neutralized reaction product is then steamed for one hour at 400° F., 82 parts of SAE 10 grade oil added, and the product filtered while hot through celite.

EXAMPLE II

A mineral lubricating oil derived from a so-called Winkler crude oil, and having a gravity of 25.6 A. P. I., Saybolt Universal viscosity at 100° F. of 285 to 300 seconds, a flash of not less than 400° F. and a pour point of −5° F. was mixed with 9% of phosphorus pentasulfide and the mixture heated at a temperature of from 100° F. to 400° F. for about three hours and maintained at the maximum temperature for an additional hour.

The phosphorus pentasulfide-lubricating oil reaction product was diluted with 50% of an SAE 20 motor oil and treated with 3% of potassium hydroxide at a temperature of 180° F. for two hours. At the end of the two hour heating period the temperature was raised to 340° F.–380° F. and maintained within this temperature range for three more hours, and the product was blown with steam within this same temperature range for three more hours and filtered.

EXAMPLE III

An isobutylene polymer having a Saybolt Universal viscosity at 210° F. of about 3000 seconds was heated with 10% of phosphorus pentasulfide at a temperature of about 380° F. for eight hours. The reaction product so obtained was cooled, 3% of KOH was added, and the mixture was heated at 180° F. for two hours. At the end of the two hour period the temperature was raised to about 340–350° F. and maintained within this temperature range for three hours. This product showed the following analysis:

	Per cent
Phosphorus	3.04
Sulfur	3.97
Potassium	2.1

The above product was diluted with an equal volume of an SAE 20 motor oil and steam blown for three and one-half hours at temperatures of from about 340–350° F.

EXAMPLE IV

The P_2S_5-olefin polymer reaction product was obtained in the manner described in Example III.

The reaction product was diluted with an equal volume of an SAE 20 motor oil and treated with 6% of KOH at a temperature of 180° F. for two hours. The temperature was then raised to about 340–350° F. and maintained within this range for three additional hours, and the product was then blown with steam while within this temperature range for three more hours.

The preferentially oil-soluble petroleum sulfonates are preferably those obtained in the treatment of petroleum oils to obtain highly refined products of the type of electrical insulating oils, turbine oils, medicinal white oils, technical white oils, etc., in which the petroleum oils are treated successively with a number of portions of concentrated sulfuric acid (i. e. above about 95% strength), or fuming sulfuric acid. A variety of sulfur-containing compounds are formed by the chemical reactions of sulfuric acid upon the oil, including sulfonic acids, organic esters of sulfuric acid, partial esters of sulfuric acid, etc. Most of these compounds are relatively insoluble in the oil under the treating conditions and separate from the oil together with unreacted sulfuric acid as a sludge, which is separated from the oil after each treatment. The sulfuric acid is usually added in "dumps" of about one-half pound per gallon of the oil, the total quantity of acid added depending upon the oil being treated and the desired final product. Usually from about three pounds to about nine pounds of sulfuric acid per gallon of oil is used. Some of the sulfonic acids resulting from the treatment of the oil with the sulfuric acid are preferentially oil-soluble and remain in the oil layer after removal of the acid sludge. These can be removed from the oil by neutralizing the acid-treated oil with an alkaline agent, such as ammonia, or an alkali metal hydroxide, preferably sodium hydroxide, to form sulfonic acid soaps or sulfonates which are then extracted from the oil by treatment with 50% to 80% aqueous alcohol solutions or other suitable means. Because of the characteristic mahogany color of these sulfonates they are known in the petroleum art as mahogany soaps. While the majority proportions of the preferentially oil-soluble sulfonates are obtained from the acid-treated oil there can be recovered from the acid sludge, by suitable solvents, preferentially oil-soluble sulfonates or sulfonic acids. The term "preferentially oil-soluble" sulfonates therefore includes the oil-soluble sulfonates obtained from both the acid-treated oil and the acid sludge.

While any of the preferentially oil-soluble sulfonates can be used, I prefer to employ those obtained from oil-soluble sulfonic acids having combined weights in the range of from about 350 to about 525, and particularly in the range of about 450 to about 500. The combining weights of the oil-soluble petroleum sulfonic acids vary with the viscosity of the oil being acid-treated and the total amount of sulfuric acid employed. To a certain degree the type of preferentially oil-soluble petroleum sulfonic acid obtained will also depend upon the type of crude oil from which the acid-treated oil is obtained. For example, the preferentially oil-soluble sulfonic acids obtained in treating a petroleum distillate having a Saybolt Universal viscosity at 100° F. of from about 60 seconds to about 230 seconds with 3 to 5 pounds of fuming sulfuric acid, have combining weights of about 430 while the preferentially oil-soluble sulfonic acids obtained when treating petroleum distillates having Saybolt Universal viscosities at 100° F. of from about 220 seconds to about 800 seconds with from about three to about nine pounds of fuming sulfuric acid per gallon of oil gave combining weights of from about 470 to about 500.

Generally we prefer to use preferentially oil-soluble petroleum sulfonates of the metals of group I of the periodic system, particularly sodium and potassium salts, although we may use sulfonates of metals or other groups of the periodic system or of ammonium or ammonia derivatives, such as amines and the like.

While as stated above, we can use metal salts of preferentially oil-soluble petroleum sulfonic acids having combining weights within the range of from about 350 to about 525, we prefer to use the metal salts of petroleum sulfonic acids having combining weights within the range of from about 450 to about 500. Specifically, we have obtained excellent results with sulfonates of the type obtainable by treating petroleum distillates of from about 200 seconds to about 800 seconds Saybolt Universal viscosity at 100° F. with from about three to about nine pounds of strong sulfuric acids, preferably fuming sulfuric acid per gallon of oil. The method of obtaining desirable soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils is illustrated by the following examples which describe the preparation of a sodium soap of the preferentially oil-soluble sulfonic acids having combining weights of about 470 to about 500.

A petroleum oil distillate having a Saybolt Universal viscosity at 100° F. of about 650 seconds is treated with from about 3 to about 6 pounds of fuming sulfuric acid per gallon of oil in one-half pound increments or "dumps." After the acid sludge from each one-half pound acid "dump" is settled and withdrawn, the next one-half pound of fuming sulfuric acid is added to the oil. The temperature of the oil before the fuming acid is added thereto is maintained below about 60° F., but due to the heat of reaction upon the addition of the sulfuric acid, the temperature of the oil may rise from about 90° F. to about 100° F. After the required total amount of fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the acid-treated oil containing oil-soluble sulfonic acids dissolved therein is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is then separated from the oil solution containing dissolved therein sodium soaps of sulfonic acids and the latter separated from the oil by extraction with alcohol of about 60% strength. The alcohol layer containing dissolved sodium sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and remove water. The crude sulfonic soap obtained in this manner contains from about 30% to about 60% sodium sulfonate, from about 30% to about 60% oil, from about 1% to about 10% water, and up to 10% inorganic salts which may be removed by the procedure hereinafter described.

The above procedure may be modified in that after the acid sludge is removed from the acid-treated oil, the oil containing dissolved sulfonic acids is extracted with about 60% alcohol to remove the sulfonic acids which may then be neutralized with sodium hydroxide and subsequently freed of the alcohol by distillation.

A preferentially oil-soluble petroleum sulfonate of similar solubility characteristics can be obtained by similarly treating a Mid-Continent crude distillate oil having a viscosity of about

350 seconds Saybolt Universal at 100° F. with a total of five pounds of fuming sulfuric acid.

Soaps of preferentially oil-soluble sulfonic acids having similar combining weights and properties are obtainable by treating a distillate having a Saybolt Universal viscosity at 100° F. of from about 500 to about 850 seconds with about 6 to 9 pounds of fuming sulfuric acid per gallon of oil.

The crude soaps of these preferentially oil-soluble sulfonic acids obtained by the procedure described above may be freed of inorganic salts by purification. This purification is preferably accomplished by dilution of the crude soap with from about ½ to about 10 parts, preferably 1 to 2 parts of 50% or higher strength alcohol, preferably alcohol of 60% to 70% strength, and allowing the salts to settle while maintaining the mixture within the temperature range of 130° F. to 175° F., preferably 155° F. to 165° F. When the salts have settled the supernatant alcohol-soap layer is separated and the alcohol is recovered by conventional distillation procedure. By this method of purification the salt content of the crude sulfonic soap can be readily reduced to 5% or less, e. g. to about 3.5%.

The percentages of sulfonic soap given herein is on a 100% soap basis.

While marked improvement in the quenching property of hydrocarbon oils is obtained by using small amounts of preferentially oil-soluble petroleum sulfonates, the improvement obtained is not permanent. Because of the high temperatures involved in quenching, hydrocarbon oils containing these preferentially oil-soluble petroleum sulfonates have a tendency to deteriorate and lose their good quenching properties. By incorporating small amounts of the neutralized reaction product of a phosphorus sulfide and a hydrocarbon of the type herein described in the quenching oil containing oil-soluble petroleum sulfonate, the product obtained retains its good quenching properties even after it has been subjected to prolonged quenching conditions.

The method of evaluating the quenching characteristics of oils is the so-called "quench ratio." The procedure used in carrying out this test is as follows:

A one inch round of cold rolled steel, preferably cold roller SAE 1020 steel, is cut into cylinders of 1¾" in length. To facilitate handling of the test pieces, a hook is inserted in the center of one end of each cylinder. Each of the cylinders are placed in a muffle furnace maintained at 1500° F. and heated for 2½ hours. 300 grams of the oil, whose quench ratio is to be determined, are measured in the 500 cubic centimeters lipless beakers and the beakers placed in the cylinders of insulating material and the temperature of the oil recorded. A steel cylinder test piece heated to 1500° F. is dipped into one of the beakers of oil for five seconds and then removed and the temperature of the oil, after thorough mixing, noted. This procedure is then repeated on a fresh sample of the oil, except that the steel cylinder is left in the oil until the temperature of the oil becomes constant, indicating a state of heat equilibrium between the oil and the steel cylinder. The equilibrium temperature is then noted. The quench ratio is then calculated, using the following formula:

$$\frac{\text{Oil temperature after 5 second quench} - \text{initial temperature}}{\text{Equilibrium oil temperature} - \text{initial oil temperature}} \times 100 = \text{Quench ratio}$$

In practice, it has been found that there is no appreciable variation in the maximum of quench temperature of various oils, and since the initial oil temperature is normally substantially room temperatures, a value of 178° F. is usually used in the denominator in the above equation for calculating quench ratios.

In order to evaluate the relative stability of the quenching oils, 250 grams of each oil is weighed in a 500 cubic centimeter lipless beaker, which is then placed in an aluminum block and maintained at a temperature of 300° F. for five days while stirring with a glass stirrer rotating at about 1300 R. P. M. At the end of this time the oil samples are removed from the aluminum block and quench ratios determined on the heated oil in the manner above described. Using the above tests, the data tabulated in Table I were obtained on the following compositions:

SAMPLE 1

Low cold test machine oil (Saybolt Universal viscosity at 100° F.=107 seconds)

SAMPLE 2

95% low cold test machine oil
5% soda mahogany soap (molecular weight of sulfonic acid=490)

SAMPLE 3

99% low cold test machine oil
1.0% KOH neutralized reaction product of P_2S_5 and an isobutylene polymer of about 1000 molecular weight

SAMPLE 4

94.1% low cold test machine oil
4.9% soda mahogany soap of Sample 2
1.0% neutralized P_2S_5—isobutylene polymer reaction product of Sample 3

SAMPLE 5

Paraffin distillate oil (Saybolt Universal viscosity at 100° F.=100–110 seconds)

SAMPLE 6

95% oil of Sample 5
5% soda mahogany soap of Sample 2

SAMPLE 7

99% oil of Sample 5
1% neutralized P_2S_5—isobutylene polymer reaction product of Sample 3

SAMPLE 8

94.1% oil of Sample 5
4.9% soda mahogany soap of Sample 2
1.0% neutralized P_2S_5—isobutylene polymer reaction product of Sample 3

SAMPLE 9

95% oil of Sample 5
2% soda mahogany soap of Sample 2
3% mixture of aliphatic alcohols, ketones, alcohol-ketones, lactones and esters obtained by controlled oxidation of petroleum hydrocarbons described in U. S. Patents 1,690,768, 1,690,769 and 1,863,004 issued to A. W. Burwell and marketed as "Alox 600."

SAMPLE 10

94.2% oil of Sample 5
1.9% soda mahogany soap of Sample 2
2.9% "Alox 600" of Sample 9
1.0% neutralized P_2S_5—isobutylene polymer reaction product of Sample 3

Table I

Sample No.	Quench—Ratio	
	Before	After
1	34	31
2	41	35
3	37	35
4	43.5	46
5	30	40
6	42	34
7	40	39
8	40	40
9	42	30
10	43	43

The effectiveness of the herein described quenching oil compositions is further illustrated by the data in Table II, representing "H values" obtained in the manner suggested by A. E. Foche in "An Evaluation of Quenching Oils," published in the A. S. M. Transactions, volume 33, (1944), pages 56 to 58. The so-called "H values" first developed by T. F. Russell and reported in the "Iron and Steel Institute Special Report," volume 14 (1936), page 194, are coefficients which represent the rate of heat transfer at the surface of the body of the metal being tested and are dependent upon the metal under consideration and upon the particular type of heating or cooling used, but are independent of the shape or the mass of the bodies studied. Since the heat diffusivity of different grades of steel is assumed to be a constant, the "H values" are assumed, in cooling rate studies, to be coefficients indicating simply the severity of the quench. The procedure for obtaining the H values described below involves the use of taper specimens cut from two-inch round hot-rolled bars from a single heat of steel. The bar stock was given a preliminary treatment consisting of heating for one hour at 1600° F. and air cooling, after which it was machined into taper specimens. The taper specimens were ½ inch in diameter at the smaller end and tapered at the rate of 0.2 inch per inch to a diameter of 1.90 inches. The 1.90 inch diameter was extended for 1 inch beyond the end of the taper, so that the total length of the speciman was 8 inches. The larger end of each speciman was drilled to a depth of about ½ inch and tapped for a ⅜ inch bolt, so that a small holder, used for handling the specimens during the quench, could be attached. All the specimens were quenched vertically with the small end down. Specimens were austenitized prior to quenching by heating for one hour at 1550° F. Each specimen was placed in a graphite cup during the austenitizing operations to reduce scaling.

The quenching equipment used consisted of a 25-gallon cylindrical utility can to which a quarter-horse power centrifugal pump was attached, and which contained a coil of ½'' copper tubing through which water might be passed as a coolant. A gas burner located under the can served as a means of heating the oil. It was found that the size of the specimen employed caused about a nine degree rise in the oil temperature during the quenching operation. The temperature of the oil was always adjusted to within ±2° F. of the values indicated later in the figures and tables before starting the quench.

Three different types of quenches were employed. First, specimens were quenched by suspending them vertically in the oil without any mechanical movement of either the oil or the specimens. This procedure is referred to as a still-oil quench. Second, specimens were quenched

with hand agitation of the specimen in the form of a figure-8 movement. Such a procedure is a common commercial method for obtaining a severe quench and is referred to herein as the figure 8 quench. The third method of quenching the specimens consisted of suspending the specimens vertically, small end down, in the center of a 3-inch-inside-diameter pipe. A centrifugal pump was used to cause an upward flow of oil through the vertical pipe. Before placing the taper specimen within the pipes, the oil flow was adjusted by means of a valve so that the free height of the overflow extended one inch above the top of the pipe. This method is referred to herein as the column quench.

After quenching specimens were ground longitudinally to a thickness of ¼ inch so that one face of the ground slice represented a plane which coincided with the original center line of the specimen. Rockwell "C" impressions were then made every ⅛ inch along the original center line of the specimen. Before making the Rockwell "C" impressions, the ground surfaces of each specimen were etched in such a way as to reveal any tempering or overheating that may have occurred during the grinding operation. In a few cases where evidence was noted of some overheating during grinding, a few thousandths of an inch of additional metal were removed and the specimen re-etched before making the hardness determinations.

Standard end-quench hardenability tests were made on the front and the back of each of the 2-inch-diameter bars received. These specimens were quenched in the standard manner after heating for 30 minutes at 1550° F. They were so machined from the original bar stock that a line on the surface of the one inch diameter end-quench hardenability bar represented the center line of the original 2-inch bar stock. After treatment, hardness readings were taken along this line which corresponded to the center line of the original bar stock.

From the hardness values obtained from the test specimens, H values were determined by the use of two graphs, published by Grossmann et al. in (1) Relation Between Jominy Test and Quench Round appears in SAE Journal, volume 49, No. 1, pages 283 to 290, 1941; and (2) The Relation of Hardenability to Quenching, published in A. S. M., 1939 (124 to 190).

The H values for the following samples were determined at various hardness levels; the data obtained are tabulated in Table II. All specimens were quenched in the oil at 110° F.

SAMPLE 1

Petroleum distillate oil having a Saybolt Universal viscosity at 100° F. of 100–110 seconds.

SAMPLE 2

94% low cold test petroleum distillate oil having a Saybolt Universal viscosity at 100° F. of 107 seconds.

5% soda soap of preferentially oil-soluble petroleum sulfonic acid of about 490 molecular weight.

1% KOH neutralized reaction product of P_2S_5 and an iso-butylene polymer of about 1000 molecular weight.

SAMPLE 3

Commercial quenching oil

SAMPLE 4

Commercial quenching oil

Table II

Sample No.	Kind of Quench	Hardness Level					
		50 R"C" [1]	48 R"C"	46 R"C"	44 R"C"	42 R"C"	40 R"C"
1	Still Oil	0.45	0.40	0.37	0.34	0.31	0.28
	Column	0.58	0.53	0.50	0.44	0.41	0.37
	Fig. 8	0.63	0.60	0.59	0.52	0.50	0.48
2	Still Oil	0.80	0.76	0.76	0.70	0.69	----------
	Column	1.05	0.83	0.78	0.76	0.76	----------
	Fig. 8	0.78	0.75	0.74	----------	----------	----------
3	Still Oil	0.38	0.36	0.34	0.32	0.32	0.28
	Column	0.53	0.50	0.45	0.42	0.40	0.36
	Fig. 8	0.53	0.50	0.46	0.44	0.42	0.40
4	Still Oil	0.39	0.37	0.36	0.33	0.31	0.29
	Column	0.51	0.49	0.47	0.42	0.39	0.37
	Fig. 8	0.59	0.55	0.55	0.47	0.44	0.42

[1] Rockwell "C" Scale.

The above data demonstrate the effectiveness of the composition of the present invention and its advantages over other known commercial quenching oil compositions. Not only are the H values of this composition (Sample No. 2) much greater than for other oils, indicating the use of this oil resulted in the most severe quench, but the three different quenching procedures caused a surprisingly small change in the H values. A quench oil which is substantially insensitive to the degree of agitation in the quenching bath is greatly desired since it will produce constant results even in the presence of poorly controlled quenching operations.

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

We claim:

1. A quenching oil composition consisting essentially of a major proportion of an oil of the group consisting of an animal oil, a vegetable oil and a viscous hydrocarbon oil having a minimum flash point of about 300° F., from about 0.1% to about 10% of a preferentially oil-soluble alkali metal petroleum sulfonate, and from about 0.5% to about 5% of an alkali metal neutralized sulfur and phosphorus-containing reaction product of a phosphorus sulfide and an olefin hydrocarbon having a molecular weight of from about 150 to about 50,000.

2. A quenching oil composition consisting essentially of a major proportion of a viscous hydrocarbon oil having a minimum flash point of about 300° F., from about 0.1% to about 10% of a preferentially oil-soluble alkali metal petroleum sulfonate, and from about 0.05% to about 5% of an alkali metal neutralized reaction product of a phosphorus sulfide and an olefin hydrocarbon having a molecular weight of from about 150 to about 50,000, said neutralized reaction product containing phosphorus, sulfur and an alkali metal as constituents thereof.

3. A quenching oil composition as described in claim 2 in which the olefin hydrocarbon is a butylene polymer.

4. A quenching oil composition as described in claim 2 in which the olefin hydrocarbon is a propylene polymer.

5. A quenching oil composition as described in claim 2 in which the alkali metal petroleum sulfonate is a sodium petroleum sulfonate.

6. A quenching oil composition as described in claim 2 in which the alkali metal sulfonate is a potassium petroleum sulfonate.

7. A quenching oil composition as described in claim 2 in which the alkali metal neutralized reaction product is a sodium neutralized reaction product.

8. A quenching oil composition as described in claim 2 in which the alkali neutralized reaction product is a potassium reaction product.

9. A quenching oil composition consisting essentially of a major proportion of a viscous hydrocarbon oil having a minimum flash point of about 300° F. from about 0.1% to about 10% of a preferentially oil-soluble alkali metal petroleum sulfonate, from about 0.05% to about 5% of an alkali metal neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and an olefin hydrocarbon having a molecular weight of from about 150 to about 50,000, and from about 0.01% to about 0.25% water.

10. A quenching oil composition comprising a major proportion of a hydrocarbon oil having a S. U. S. viscosity at 100° F. of from about 80 seconds to about 200 seconds and a minimum flash point of about 300° F., from about 0.1% to about 10% of a sodium soap of a preferentially oil-soluble petroleum sulfonic acid having a combining weight of from about 450 to about 500, and from about 0.5% to about 5% of the phosphorus, sulfur, and potassium-containing neutralized reaction product of a phosphorus pentasulfide and a butylene polymer having a molecular weight of about 1000.

11. A quenching oil composition as described in claim 10 which contains from about 0.01% to about 0.25% of water.

12. A quenching oil composition consisting essentially of a major proportion of a viscous hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of about 107 seconds, 5% of a sodium soap of a preferentially oil-soluble petroleum sulfonic acid having a molecular weight of about 490, and about 1% of the KOH neutralized reaction product of P_2S_5 and an isobutylene polymer of about 1000 molecular weight.

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