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QUENCHING STEEL

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This invention relates to quenching metals, to quenching mediums for use in such quenching methods, and to the resulting quenched metals themselves, in producing metals which are more uniform in character, of increased hardness, toughness, and ductility as compared with metals quenched by prior art methods.

Although various practices have been developed in the metal art for imparting hardness and strength to metals, one of the most important is quenching of heat-treated metals from above their critical temperature in liquid mediums. The quenching operation essentially involves immersing metals which have been heat-treated above the critical temperature of the metal, into suitable quenching medium in order to establish certain improved physical structures in the metal as uniformly as possible, upon which the hardenability and strength of the metal depend, and without setting up great internal stresses and strains in the metal, so as to avoid the possibility of distortion, warping, and, in some cases, even cracking of the quenched metal.

Hardenability is imparted to metals when rapidly cooled from above their critical temperature so as to allow the transformation of the physical structure of the metal. In connection with steels for example, there is the transformation of the physical structure of the metal from austenite and cementite, which is a composition of iron and carbon dissolved in austenite, into hard martensite and other hard structures. This transformation should be conducted at as low a temperature as possible and in the shortest time interval, and having attained this range, the heat transfer from the metal surface to the liquid medium should be as continuous and uniform as possible in order to obtain metals of greater and more uniform hardenability. With slow cooling, carbide precipitates from austenite during transformation into ferrite to give a soft pearlite structure. However, when metals are rapidly cooled, the carbide does not precipitate out and most of it is held in solid solution in the transformed austenite into martensite or other hard structures. A principal object of quenching, therefore, is to produce these physical transformations without distortion, warping, or setting up such great internal stresses in the metal as would result in cracking, and at the same time obtain maximum and as nearly as possible uniform hardenability in the metal.

The conventional art of quenching heat-treated metals from above their critical temperature in order to induce hardenability by means of water and other mediums such as brines and caustic soda solutions, is a well established practice. Although quenching heated metals in aqueous mediums imparts maximum hardenability, warping, distortion, brittleness, uneven hardness, and

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even cracking of the metals frequently occur. These disadvantages apparently are caused by pockets formed by vapors of the solution or by its condensation on the quenched object which create marked differentials in the hardness of the metal surface. These areas may either be localized or generally diffused. The vaporous interface which forms between the metal surface and quenching medium acts as an insulator, thus preventing uninterrupted desired rate of heat flow from the metal surface into the liquid medium. This vaporous insulating interface inhibits heat diffusivity from the core of the metal through the hardened metal surface into the liquid medium, thus trapping the heat in the metal and causing a slower rate of cooling, which results in different physical structure formation from that formed at the rapidly cooled surface. Such uneven cooling process produces metals having hardnesses which are not uniform throughout the metal or even at its surface and which causes brittleness in isolated areas or even over the whole area. In addition, drastic aqueous quenching results in warping, distortion, and cracking of the metal thus treated.

Oil emulsions or various oils such as fish and marine oil, animal oils, mineral oils, and their mixtures, have supplanted aqueous quenching mediums in alleviating the defects generally produced in metals by aqueous quenching. Although quenching oils and oil emulsion mixtures in part relieve the internal stresses formed during hardening, and although brittleness is reduced, metals quenched in such mediums are usually softer than those quenched in aqueous mediums, since the quenching speed of such compositions is substantially slower, thus inhibiting or retarding the formation of hard martensite, spheroids and other hard structures. Furthermore, as in connection with aqueous quenching mediums, a persistent vaporous interface forms between the metal and the liquid, which acts as an insulator and retards the flow of heat from the surface of the metal into the liquid. In addition, oil and/or oil emulsions tend to oxidize, form sludge, thicken, break down, and decompose at elevated temperatures, which greatly decrease the life of the composition, make it troublesome to use, and produce results which are not uniform.

Among the objects of the present invention is the development of methods for quenching metals which give the desired improved properties as to hardness, etc., and reduce the defects of prior art quenching methods to a minimum.

Further objects include the production of mediums which enable such quenching operations to be carried out.

Further objects include quenching mediums having a rapid initial cooling rate and thereafter a uniform and continuous rate of cooling, so as

to produce a metal of improved hardness, ductility, and strength, etc.

Further objects include the production of oil and oil emulsion quenching mediums which effect greater and more uniform hardness in metals than any known commercial oil composition and which approach the hardnesses in metals which result from aqueous quenching.

Further objects include oil and oil emulsion quenching compositions which are highly stable over wide temperature variations and long periods of use and which are not corrosive to the metal with which they are in contact, but rather act as corrosion inhibitors.

Still further objects and advantages of the present invention will appear from the more detailed description set forth below, it being understood that this more detailed description is given by way of illustration and explanation only, and not by way of limitation since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present invention metals are quenched in a quenching medium containing a minor amount of an organic sulfonate. Individual organic sulfonates or complex mixtures of organic sulfo compounds may be utilized. They are desirably employed in mediums of oil and/or water and/or emulsions of oil and water. The quenching medium may be so prepared as to have either oil or water as its continuous phase. The phase selected will have an effect upon the ultimate maximum physical properties of the quenched metal. Generally an object quenched in water is much harder and more brittle than the same object quenched in oil. However, with a combination of oil in water or water in oil emulsions, the desirable properties may be enhanced without the disadvantageous features. To such compositions various additives may be incorporated for producing particular effects, more particularly fatty acids and/or organic amines or combinations of fatty acids and organic amines may be added to these compositions to impart beneficial effects to the quenching medium as well as to the metal treated.

The organic sulfonate employed may be aliphatic, aromatic, heterocyclic, or mixtures of any of these various organic sulfonates. A particularly desirable sulfonate that may be employed in accordance with the present invention includes the sulfonates derived from treatment and purification of petroleum oils with sulfuric acid. The conventional method of recovering sulfonates as by-products during the refining of petroleum distillates is to dilute the sludge with a hydrocarbon oil. The mahogany acids remain in the resulting oil layer and are separated from the sludge layer which contains the green acids. The oil layer can be washed with aqueous alcoholic solutions which remove the mahogany acids; or it may be treated with alkali and the sulfonic acids recovered with alcohol as mahogany salts. The sludge may be boiled with water and the dilute acid recovered. The supernatant layer may then be neutralized and the residual oil extracted with naphtha, or other suitable solvent or method for producing the organic sulfonate. The neutralized sulfonate is purified by washing with acid or extraction with alcohol, or in any other suitable manner. The sulfonates thus formed are commonly referred to in the art as mahogany sulfonates, and various salts of such sulfonates such

as the alkali, alkaline earth, and heavy metal salts of petroleum sulfonic acids, water or oil-soluble, may be utilized in accordance with the present invention.

Other desirable sulfonates that may be employed include esters of sulfo-dicarboxylic acids, polyalkylated naphthalene sulfonates, polyalkylated naphthalene sulfonate-formaldehyde condensation products, polyalkylated diphenylsulfonates, higher sulfated secondary alcohols, higher alkyl sulfated alcohols, sulfonated castor oil, sodium taurocholate, etc. For example, the following compounds have been found satisfactory: the esters of sulfo-succinic acid, formaldehyde condensation products of di-isopropylated naphthalene B sulfonic acid, di-secondary butyl naphthalene sulfonate, sodium tetrahydronaphthalene B sulfonate, organic petroleum sulfonates, etc. In illustrating the invention below, the mahogany sulfonates will be utilized since they are readily available and are less expensive, and therefore, are desirable in producing quenching mediums in accordance with the present invention.

Various types of oils may be utilized in compounding the quenching mediums of the present invention, particularly petroleum oils, petroleum oil fractions and petroleum oil distillates. Mineral oils of various types having relatively high flash and fire points, and that are substantially heat and sludge resistant may be used as diluents for the quenching bases of this invention. Such oils, for example, may be of the naphthenic or paraffinic type, and desirably have a viscosity at 100° F. of from 50 to 1000 S. U. V.

Organic amines that may be added to the quenching mediums may be any type of organic amine including aliphatic, aromatic, carbocyclic, alicyclic, and heterocyclic amines, among which may be mentioned alkylamines, alkyl polyamines, alkylolamines, polyalkylene polyamines, alicyclic amines, aralkylamines, heterocyclic basic nitrogen compounds, etc. Representative examples of such amines are diethylamine, monoamylamine, di-amylamine, and tri-amyl amine, di-n-butylamine, monobutylamine, undecyclic amine, lauryl amine, myristicamine, palmitylamine, stearylamine, mono-, di-, and tri-ethanolamine, quaternary ammonium compounds, laurylolamine, palmitylolamine, stearylolamine, ethylene diamine, diamino-isopropanol triethylene tetramine, cyclohexylamine, dicyclohexylamine, benzylamine, morpholine, piperidine, pyridine, quinoline, cephalin, lecithin, etc., as well as materials like "Alkaterge-O."

Fatty acids that may be employed are the higher fatty acids both saturated and unsaturated, particularly those that may be produced or obtained from vegetable and animal glycerides and they may be used as individual fatty acids or as complex mixtures thereof as derived by the saponification of the oils and fats, exemplary acids and mixtures including oleic, myristic, lauric, undecyclic, stearic, palmitic, ricinoleic, abietic, linoleic, peanut-oil fatty acids, soya bean oil fatty acids, hydrogenated soya bean oil fatty acids, hydrogenated fish oil fatty acids, blown and boiled acids, etc. Abietic acid is exemplary of the acids obtainable from natural resins including rosin, etc., and may also be used as such or in hydrogenated condition, or mixed with fatty acids, etc.

Various mixtures of organic sulfo compounds

admixed with fatty acids and/or amines when desired, and diluted with mineral oil or formed into emulsions have been found to possess the unusual property of cooling heat-treated metals rapidly initially so as to establish those physical structures in the metal which impart maximum hardness, ductility, and strength, as well as subsequent slower but uniform cooling which reduces to a minimum internal stresses caused by the quenching operation. Compositions of this invention possess the combined desired properties of aqueous and oil quenching mediums and more ideally approach these properties than any known quenching material as illustrated hereinafter.

The unusual quenching properties of organic sulfo containing quenching mediums appear to be due to the initial high heat absorptive capacity of such mediums, which causes an extremely rapid cooling of the metal, resulting in great hardness and sharply reducing resistance to unit heat flow. This reduction may be due partly to elimination of an insulation film and/or improvement in the metal-to-medium interface, minimizing stresses and strains in the metal. The liquid medium of this invention and the surface of the metal approach a state of solid-liquid continuous phase relationship throughout the quenching time. This appears to be due to a chemical or physio-chemical reaction which takes place on the metal surface, bringing about a nearly continuous phase resulting in an almost uninterrupted rate of heat flow from the heated metal into the cooler quenching mediums of this invention. Thus, by maintaining this phase relationship, heat continues to be lost at the surface of the metal at a rate proportional to the difference in temperature between the surface of the metal and cooler quenching medium, resulting in more uniform and harder metal. Regardless, however, of whether these explanations theoretical or otherwise, may be the explanation as to why the improvements take place, unique results have been obtained in practice in utilizing the quenching mediums of the present invention.

The following examples will illustrate the invention and the unusual improved results obtained, quenching compositions that may be employed in accordance with the present invention and their comparison with known prior art types of quenching mediums. The proportions, type of sulfonate used, as well as other additives mentioned in the examples given below are not to be construed as limitations. The examples illustrate wide ranges of mixtures, proportions, and applicability of quenching mediums of this invention.

In these examples, the invention is particularly illustrated by its application to the improvement in properties of steels. While various metals may be treated, the application of the invention to steels particularly illustrates the unique results obtained. The steel treated may be of any desired type such as those known in the art as NE 8630, NE 8650, SAE 1065 steels, SAE 1010, SAE 4065, SAE 4067, 6322, 6150, 9442, and 4140, as well as other alloy steels may be treated in accordance with the present invention utilizing the improved quenching mediums and operations of the present case to produce the beneficial effects sought.

EXAMPLE 1

A 1:1 mixture of mahogany sulfonate and mineral oil was diluted with 40 parts by weight of mineral oil and used as a quenching medium for SAE 1065 steel bars of ⅝–⅞ inch diameter and 36–72 inches in length. The steel was heated to about 1700° F. and quenched from about 1500–1575° F. in the liquid medium for about 4 minutes in order to complete the quenching operation. Hardenability of the metal was determined by the Rockwell "C" scale and Brinell tests. Improvement in hardness and tensile strength of the metal when using the composition as compared with a prior art base standard quenching oil is illustrated in the following table.

Table I

Quenching Medium	Rock. Hard.	Brinell	Life of Oil	Remarks
Standard (see below)	39	363	3 weeks	Warping, deforming, cracking from 20–50%.
1 part mahogany sulfonate; 40 parts base quenching oil.	47 to 55	444 to 555	9 months	No dimensional changes; no warping, cracking, or deforming; no surface checks.

EXAMPLE 2

The same composition and dilution as given in Example 1 above was used as a quenching medium for SAE 1050 steel flywheel ring gear stock ½ inch square, quenched at 1550° F. When this gear is quenched in the base oil, the hardness on the Rockwell "C" scale in the same cross-section varies from 34–53; when the same gear is quenched in the medium described in this Example 2, the hardness on the Rockwell "C" scale in the same cross-section varies only from 55–58.

EXAMPLE 3

Using the same quenching composition as that given in Example 1 above, namely, a composition consisting of equal parts by weight of mineral oil and mahogany sulfonate, but diluting this composition of Example 1 with 10, 20, 50, 100, and 200 parts by weight of the base blending mineral oil, NE 8630 and NE 8650 steel bars 1½ inches rd. x 6 inches long were quenched from 1550° F. in the stated compositions, and hardenability results compared with a prior art standard quenching blending oil medium. The results are given in Table II below for the NE 8630 bar.

Table II

	BQO	½	1	2	5	10
Surface	36	41	41½	43½	45	46
1/16" deep	34	36	37	38	41	42
¼" deep	33	34	35	36	36	38
⅜" deep	30¼	31	31½	32½	33½	35
½" deep	30	30¾	31	32	32	34¼
⅝" deep	29	30¼	30½	31½	32	31
¾" deep	28	30	30½	31	32	30

In the above table and in the tables which follow BQO stands for base quenching oil used in production as a control for the rest of the tables. It is a blending mineral oil having a viscosity of about 50 or more Saybolt units/sec. at 100° F.

The initial mixture 1:1 of mineral oil and mahogany sulfonates is merely for convenience of handling since the sulfonates are very viscous. Other ratios may be used of the oil to dilute the sulfonates, and various proportions of ultimate dilutions are given in the tables. ½ stands for the base quenching oil and ½% of the composition mentioned in Example 1; 1 stands for the base quenching oil and 1% of the composition mentioned in the example; 2 stands for the base quenching oil and 2% of the composition mentioned in the example; 5 stands for the base quenching oil and 5% of the composition mentioned in the example; and 10 stands for the base quenching oil and 10% of the composition mentioned in the example. In carrying out the procedure, 1½ inch round rods of NE 8630 steel were normalized at 1675° F. and quenched at 1550° F., the quenching bath temperature being 110 to 120° F. From the same heat steel, under the same conditions and at the same time the control bars were quenched in the BQO=blending quenching oil above without the additive of the present invention, and the results compared as shown in the table. The numbers in the tables refer to Rockwell "C" hardness in depth of cross-section of the quenched rods. Similarly improved physical properties were obtained for the NE 8650 steel.

EXAMPLE 4

This quenching base consisted of:

7.5 parts by weight of oleic acid
50.0 parts by weight of mahogany sulfonate
42.5 parts by weight of mineral oil

It was diluted in the same proportions with mineral oil and used as a quenching medium for NE 8630 and NE 8650 steel bars under the same conditions as referred to above in the preceding examples. The results obtained are shown in Table III below for the NE 8630 steel, similarly improved physical properties having been obtained for the NE 8650 steel.

Table III

	BQO	½	1	2	5	10
Surface	36	43	43½	44½	45½	46½
⅛" deep	34	37	39½	43	43	40½
¼" deep	33	34	35½	38	37	36
⅜" deep	30¼	32	32½	34	34	34½
½" deep	30	32	32	32½	33	33
⅝" deep	29	31½	31½	32	33	31
¾" deep	28	31	31	31½	33	31

EXAMPLE 5

Using similar steel bars 1½ inches in diameter, the composition of Example 2 was modified by the addition of minor amounts of oleic acid and triethanolamine to a mixture of mineral oil and mahogany sulfonate and used as a quenching medium under the same conditions as indicated in Examples 1 and 2. Specifically, this quenching composition consisted of:

5.53 parts by weight of oleic acid
3.51 parts by weight of triethanolamine
47.90 parts by weight of mahogany sulfonate
43.10 parts by weight of mineral oil

This base quenching composition was diluted with 10, 20, 50, 100 and 200 parts by weight of mineral oil, and the results obtained are recorded below in Table IV.

Table IV

	BQO	½	1	2	5	10
Surface	36	44	44	45	47	48
⅛" deep	34	40	41	44½	44½	43
¼" deep	33	35	36	40	38	37
⅜" deep	30¼	32½	33	35½	35	35
½" deep	30	32	32	33	34	34
⅝" deep	29	31¾	32	32½	35	32½
¾" deep	23	31¼	31½	32	34½	32½

Likewise improved physical properties were obtained for the NE 8650 steel.

EXAMPLE 6

Modifying the base quenching composition still further by adding an excess of amine, the composition was diluted with mineral oil in the same proportions as indicated in the above examples and used in quenching mediums for NE 3630 and NE 8650 steel bars under the same conditions as referred to above, and the results show in Table V below for the NE 8630. Similarly improved physical properties were obtained for the NE 8650 steel. Specifically, the base quenching composition comprised:

5.5 parts by weight of oleic acid
8.5 parts by weight of triethanolamine
45.0 parts by weight of mahogany sulfonate
45.0 parts by weight of mineral oil

Table V

	BQO	½	1	2	5	10
Surface	36	45	46	46	48	49
⅛" deep	34	41½	42	45	45	44
¼" deep	33	36	37	41	38½	38
⅜" deep	30¼	33	34	36½	36	35½
½" deep	30	32½	33	34	35½	34½
⅝" deep	29	32½	33½	33	35½	33½
¾" deep	28	32	32½	33	35½	33½

Reference to Tables II, III, IV and V indicates an overall improvement in hardenability of metals quenched in the compositions of the present invention, even when dilutions of 200 to 1 were used as compared with prior art standard quenching oils and the tables clearly illustrate the improvements obtained. Using 20:1 dilutions of compositions of this invention, for example, Rockwell "C" hardness for NE 8630 steel of from 47 at the surface to 34 at the core, as compared with about 36.5 at the surface and about 28 at the core when using straight quenching oil, is readily obtainable. Improved results were also observed for NE 8650 steel.

When the composition of Examples 1, 2, 3 and 4 is prepared with hydrophilic organic sulfonates in a water medium, corresponding physical properties are materially enhanced without the disadvantages that water alone as a quenching medium would produce. Similarly, if the composition of Examples 5 and 6 are used in a water medium, there is corresponding enhancement of the physical properties without the disadvantages incurred by water quench alone. When the respective compositions of Examples 1 through 6 are mixed with water and oil, the corresponding physical properties fall within the upper and lower limits of the water quench and oil quench.

If it is desired to approach those physical properties obtained by the water quench composition of this invention, then the quenching

medium is prepared so that the continuous phase is the water and the discontinuous phase is the oil. Such a composition is illustrated by the following:

EXAMPLE 7

5 parts of oleic acid
8 parts of triethanolamine
50 parts of organic sulfonate
34 parts of mineral oil
3 parts of sodium acetate
1900 parts of water

Where it is desired to approach those physical properties obtained by the oil quench composition of the present invention, then the quenching medium may be prepared so that the continuous phase is the oil and the discontinuous phase is the water. Such a composition is illustrated by the following:

EXAMPLE 8

5 parts of oleic acid
3 parts of butylamine
47 parts of organic sulfonate
945 parts of mineral oil
1000 parts of water

In producing the composition as enumerated above, any desired order of mixing the ingredients may be employed. More particularly the sulfonate admixed with oil may be further diluted with the mineral oil component, and the other components then incorporated as desired. Where some materials are soluble in water, they may be dissolved in the water when the latter is used before the water is incorporated with the other components. Emulsions, dispersions and suspensions may be produced by the usual methods from these stated compositions.

A water quench composition in accordance with the present invention, with physical properties approaching more nearly that of conventional water quench, yet reducing the stresses and strains usually obtained thereby, is illustrated as follows:

EXAMPLE 9

17 parts triethanolamine
28 parts oleic acid
100 parts organic sulfonates
2 parts sodium acetate
2000 parts water

Parts are by weight. The materials may be mixed together in any desired way to give the final composition.

An important accomplishment of the present invention is the elimination of quenching cracks, warping, and distortion of metals treated with quenching compositions. Thus the steel bars referred to in Example 1 above, when quenched in a standard quenching medium, resulted in from 20 to 50% rejects due to warping and cracking. Utilizing the compositions of the present invention for quenching baths, this problem is entirely eliminated under actual production conditions for long periods of time.

In Examples 1 through 9 there are shown respective quenching mixtures produced in accordance with the present invention, containing sulfonates, sulfonates and fatty acids, and sulfonates, fatty acids, and amines, and that table indicates that the hardness is only moderately influenced by the respective compositions. However, these compositions are beneficial in modifying the quenching medium when it is mixed with water or oil or a combination of both. In addition, the added components even though they may not materially affect the hardness, as for example, in the case of NE 8650 in which the hardness throughout the 1½ inch cross-section of the quenched metal is almost a straight line, act to reduce cracking, checking, warping to a minimum, and in addition act as inhibitors of oxidation and corrosion and secure stabilization of the mixture.

It should be kept in mind that other factors which are not controllable by quenching mediums, also influence the hardenability of metals. Thus there must be taken into account the thermal diffusivity of the metal which is a thermal property of each individual steel and can be defined as the facility with which heat is transferred within the metal itself at different temperature levels. Furthermore, the uniformity and depth of hardening depend upon the austenite composition of the metal, the grain size of the austenite, and the amount and distribution of insoluble particles in the austenite. The size of the specimen treated and its surface condition are also important factors which govern the hardenability of the metal. However, considering these inherent factors of the metal as constant, for any particular given metal, the quenching composition of this invention approaches more closely than any known quenching material the ideal results desired in the hardening of metals.

The organic sulfonates and/or mineral oil and/or fatty acids utilized in accordance with this invention may as illustrated above be used per se, or may be reacted or treated in other ways in order to modify them for utilization in quenching mediums. Thus they can be reacted with phosphorus sulfides such as P_2S_5, P_4S_3, P_2S_7, etc., and/or reacted with oxidizing agents such as air, potassium permanganate, hydrogen peroxide, phosphorus pentoxide, phosphorus trioxide, phosphorus tetraoxide, ozone, chromates, organic peroxides, such as benzoyl peroxide, lauroyl peroxide, etc., ultra violet rays, X-rays, actinic rays, and other oxidizing agents, in order to impart additional beneficial properties to the quenching medium as well as to the metal treated. Thus the sulfonate, the fatty acid, and the mineral oil may be treated separately or in combination by any of the treatments set forth above, as for example, with phosphorus sulfide at an elevated reaction temperature and the complex reaction base mixture diluted with suitable amounts of mineral oil or water and utilized in accordance with the present invention. The phosphorization and sulfurization treatment may be carried out by heating the stated ingredients or mixtures thereof with any of the stated phosphorus sulfides at elevated temperatures as from 150 to 500° F. for a length of time usually several hours, sufficient to introduce substantial amounts of phosphorus and sulfur into the materials treated or to modify such materials in important directions. The oxidation treatment referred to may be carried out at an elevated temperature, of for example, from about 200 to about 500° F. with any of the stated oxidizing agents for a length of time usually several hours to produce a resulting product which contains combined oxygen in an amount of at least 1%. Or the sulfurization and phosphorization treatment may be applied to the sulfonates or amines or fatty acids or mixtures containing them either in the presence of or in the absence of the mineral oil, and then followed by an oxidation treatment of the character set forth

above, or the oxidation treatment may first be applied to any of the stated ingredients or mixtures containing them and then subjected to the phosphorization and sulfurization treatment. Treatments of this character produce complex and far reaching changes in the ingredients that result in materials of particular value for utilization in accordance with the present invention.

The invention has been illustrated by the treatment of steels, alloy steels, etc., as exemplary of the new and unexpected results which are obtainable in the treatment of any metals or their alloys which during processing require a quenching operation. The quenching bath employed will vary within the limits taught herein depending on the metal being treated, the conditions under which it is treated, and the particular effects sought. In general it may be said that in producing compositions suitable by dilution for quenching baths in accordance with the present invention, proportions of ingredients will fall within the following limits in the production of the primary bath: sulfonates, from a fraction of one to one hundred percent; mineral oil, from a fraction of one percent to about 99¾%; fatty acid, from ¼% to 60%; and amine, from ¼% to about 40%; the percentages being by weight. The primary baths are then utilized for making the final baths. For steels, the amount of sulfonate in the final treatment medium will ordinarily be less than 15% with or without corresponding amounts of the other additives.

Having thus set forth my invention, I claim:

1. The method of hardening steels which are hardenable by heating and quenching which comprises heating such steel to a temperature above its critical temperature and quenching such heated steel by immersion in a quenching liquid medium containing a minor amount of an organic sulfonate the quenching medium being selected from the group consisting of oil, water, and oil-water emulsions.

2. The method of hardening steels which comprises heating steel which is hardenable by heating and quenching to a temperature above its critical temperature and quenching the heated steel by immersion in a mineral oil quenching medium containing a minor amount of an organic sulfonate.

3. The method of quenching steels which comprises heating the steel to a temperature above its critical temperature and quenching the heated steel by immersion in an aqueous emulsion quenching medium containing a minor amount of an organic sulfonate the emulsion being a mineral oil-water emulsion.

4. The method of quenching steels which comprises heating steel which is hardenable by heating and quenching to a temperature above its critical temperature and quenching the heated steel by immersion in a quenching liquid medium containing a minor amount of oil-soluble petroleum sulfonates the quenching medium being selected from the group consisting of oil, water, and oil-water emulsions.

5. The method of hardening steels which comprises heating steel which is hardenable by heating and quenching to a temperature above its critical temperature and quenching the heated steel by immersion in a mineral oil quenching medium containing a minor amount of petroleum sulfonate, and minor amounts of a higher fatty acid and of an organic amine.

6. The method of quenching steels which are hardenable by heating and quenching which comprises heating such steel to above its critical temperature and quenching such heated steel by immersion in a quenching medium containing from 0.50% to 15% of an organic sulfonate the quenching medium being selected from the group consisting of oil, water, and oil-water emulsions.

7. The method of quenching steel which comprises heating steel which is hardenable by heating and quenching to above its critical temperature and quenching the steel at a temperature above 1500° F. into a quenching medium containing from 0.50 to 15% of an organic sulfonate the quenching medium being selected from the group consisting of oil, water, and oil-water emulsions.

8. The method as set forth in claim 7 in which the quenching medium comprises a major amount of mineral oil and from 0.50 to 15% of petroleum sulfonates.

9. The method as set forth in claim 8 in which the quenching medium contains a minor amount but less than the amount of mahogany sulfonate, of a higher fatty acid and an organic amine.

10. The method as set forth in claim 9 in which the fatty acid is oleic acid and the amine is triethanolamine.

11. The method as set forth in claim 6 in which the quenching medium comprises a major amount of water and the organic sulfonate is mahogany sulfonate.

12. The method as set forth in claim 11 in which the quenching medium contains a minor but less than the amount of mahogany sulfonate, of a higher fatty acid and an organic amine.

13. The method as set forth in claim 12 in which the fatty acid is oleic acid and the amine is triethanolamine.

14. The method as set forth in claim 6 in which the quenching medium comprises a major amount of an oil and water dispersion.

15. The method as set forth in claim 7 in which the quenching medium comprises a major amount of an oil and water dispersion.

16. A quenching oil composition consisting essentially of a major proportion of a hydrocarbon oil having a high flash point and a viscosity of 100° F. of from 50 to 1000 S. U. V. and from about 0.50% to about 15% of an oil soluble petroleum sulfonate, in which the composition contains a minor amount but less than the amount of petroleum sulfonate, of a higher fatty acid and an organic amine.

17. The composition as set forth in claim 16 in which the fatty acid is oleic acid and the amine is triethanolamine.

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