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QUENCHING PROCESS

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ABSTRACT OF THE DISCLOSURE

In the quenching of a metal wherein metallurgical changes in the metal are brought about by rapidly cooling the heated metal by immersion in a liquid quenching bath, improved cooling rates and improved metal hardening characteristics are obtained by using as the quenching bath an oil having a flash point of at least 250° C. to which has been added from about 2 to about 15 weight percent, on a total composition basis, of a sulfur-containing derivative of an alkali metal salt or alkaline earth metal salt of an alkyl phenol, an alkyl thiophenol, or an alkyl phenol thioether, wherein the alkyl groups have from 5 to 30 carbon atoms. The sulfur-containing derivative can be obtained by reacting the metal salt with elemental sulfur or by reacting the metal salt with a phosphosulfurized hydrocarbon such as phosphosulfurized polyisobutylene. Additional metal over and above that accounted for by the said metal salt may be present, e.g. in the form of dispersed metal carbonate. The quench oil can also contain from 2 to 15 weight percent of metal organic sulfonate.

This invention relates to a process for quenching metals, especially the mar-quenching of low alloy steel through hardening; and low alloy case hardening steel.

With ever-increasing competition many industries, especially the motor car industry, have been seeking ways to cheapen their process of producing high quality hardened components such as gears, or pinions. In particular attention has been directed towards the production of high quality products from the cheaper and more readily available low alloy steels, such as B.S. En 31, 32, 35, 42, 44, 351, 352, 353, 363 and SAE 1019, 4620, 8615, 8617, 52100 and 8620 steels. These products are nearly always produced by forming accurately, then hardening by heating the metal, e.g. steel, to high temperature and then plunging the metal rapidly into a bath of a liquid maintained at a certain temperature or within a certain temperature range. In order to reach the required degree of hardness without distortion, cracking or wide variations in hardness from batch to bath, and to obtain a hardened metal of consistent and satisfactory core hardness, and to obtain satisfactory oil life, it is necessary that the process be carefully controlled and that the quenching liquid should meet fairly stringent requirements. The liquid should have a high flash point, good thermal stability, long life, very high cooling rate over the critical temperature range down to about 500° C., good metal hardening characteristics and should not cause thick deposits to be left on the metal after removal from the quenching bath. The liquid should also be capable of rapidly absorbing heat from the hot metal so that the quenching time is reduced. Hitherto, the quenching of metals using the quenching oils on the market has not met all these stringent requirements. However, a process has now been discovered whereby many if not all the previous difficulties have been overcome.

According to the process of the invention a metal is quenched or press quenched by heating the metal to an elevated temperature, and thereafter transferring the

metal into a bath or mould containing a liquid maintained at a temperature lower than the elevated temperature, wherein the liquid comprises a major proportion by weight of an oil, e.g. a hydrocarbon oil, and a minor proportion by weight of a phenol-based detergent additive (as hereinafter defined).

The process of the invention can be applied to the quenching of any metal or metal alloy, but is especially suitable for quenching through or case hardened steels, e.g. a steel having a carbon content, at least at the surface, of about 0.9% by weight. Other suitable metals include aluminum alloys.

The elevated temperatures to which the metal is first heated and soaked will depend on the nature of the metal, but generally this temperature will be at or above the temperature where the impurities or alloying elements are in solid solution. Thus, in the case of carbon steel this elevated temperature will be above 800° C. and often about 900° C., whereas with aluminum alloys, e.g. duraluminium, this elevated temperature will be of the order of about 500° C.

The temperature of the liquid in the bath into which the metal is plunged will vary according to the treatment it is desired to give to the metal. Thus, in the case of carbon steel (e.g. 0.9 to 1.2% by weight carbon) if it is desired to marquench the steel, the temperature of the liquid in the bath will be maintained at about 150° C. to 250° C., e.g. about 200° C. depending upon the Ms point of the particular steel. If however, it is desired to "cold" quench the steel the temperature of the liquid will be from ambient to about 60° C. "Cold" quenching of steel will normally result in a more rapid quench than marquenching, but there will be more difference in mechanical properties between the core and case of the metal. For warm quenching of steels the temperature of the liquid will usually be from 60° C. to 250° C. When quenching aluminium alloys, the temperature of the liquid in the bath will often be about ambient.

The metal should be transferred or plunged into the bath as quickly as possible. The bath may be a tank or any receptacle suitable for containing the liquid and also large enough to accommodate the metal which is being quenched. Generally the metal will completely immersed in the liquid whilst it is being quenched until the case/core temperature differential is small enough to prevent internal stresses being set up during subsequent conversion to martensite (in the case of steel) or mixed structures on cooling in air or by water spray to ambient temperature. The quench bath may be covered or uncovered, and may be maintained under an inert atmosphere preferably an endothermic gas.

The oil may be a synthetic oil, e.g. a polyglycol ether or ester, but is generally a hydrocarbon oil. The hydrocarbon oil is preferably a distillate mineral oil of medium viscosity. For cold quenching, naphthenic or mixed base distillates of medium to low viscosity are suitable. For marquenching especially suitable mineral oils are paraffinic distillates having a KV at 210° F. of between 9.0 and 14.0, e.g. about 12.5, a viscosity index of between 80 and 105, e.g. about 100, and a flash point of at least 250° C., e.g. about 280° C.

In general it has been found that close cut high flash point (e.g. above 250° C., and preferably above 270° C.) middle distillates are the most suitable hydrocarbon oils.

The phenol-based detergent additive contained in a minor proportion in the hydrocarbon oil is defined as the reaction product of sulphur or a sulphur-containing compound with either (1) an alkyl phenol or alkyl phenol sulphide and an alkali metal or alkaline earth metal base, or (2) an alkali metal or alkaline earth metal alkyl phenate or alkyl thiophenate.

Thus, the detergent additive may be alkaline earth metal (e.g. barium) sulphurised phenate or an overbased alkaline earth metal (i.e. barium) sulphurised phenate. Such phenates are prepared by reacting an alkaline earth metal alkyl phenate with elemental sulphur to give a complex reaction product, free alkyl phenol or volatile material in the reaction product preferably being removed by steam distillation. The alkyl phenate can be prepared by reacting the corresponding alkyl phenol, e.g. octyl or di-octyl phenol, with an alkali metal base or preferably an alkaline earth metal base, e.g. barium octahydrate. The reaction between the phenate and sulphur is conducted at elevated temperature, and preferably in the presence of an inert gas, e.g. nitrogen. A preferred method of making this type of phenol-based detergent additive is described in British patent specifications 697,461 and 720,372.

The more preferred types of phenol-based detergent additives are those prepared by reacting either (1) an alkali metal or alkaline earth metal base with an alkyl phenol or alkyl phenol sulphide and a phosphosulphurised hydrocarbon in the presence of a diluent oil, or (2) an alkali metal or alkaline earth metal alkyl phenate or alkyl thiophenate with a phosphosulphurised hydrocarbon in the presence of a diluent oil. In both cases (1) and (2) it is preferable if carbon dioxide is blown into the reaction mixture whilst the reaction takes place.

Suitable alkyl phenols or alkyl phenol sulphides include mono or polyalkyl compounds in which each of the alkyl groups contains between 5 and 30, e.g. 8 to 26 carbon atoms. Particularly suitable phosphosulphurised hydrocarbons are phosphosulphurised polyolefins, e.g. polybutene, having a molecular weight of from 100 to 50,000 e.g. about 900. Methods of preparing these phenol-based detergent additives are described in British Patent specifications 921,124; 940,175; 958,520; 970,786; 867,800 and 887,334. This type of phenol-based detergent additive, i.e. prepared by a reaction involving a phosphosulphurised hydrocarbon, is preferably highly basic, e.g. having an alkalinity index greater than 50. This of course may be achieved by ensuring that there is excess base in the reaction mixture. Generally, it is preferable if these additives are derived from alkaline earth metal base, especially from barium pentahydrate or barium octahydrate.

The quantity of phenol-based detergent additive incorporated in the quenching liquid is preferably less than 20% by weight, and a suitable amount has been found to be about 15% by weight, based on the combined weight of hydrocarbon oil and phenol-based detergent additive.

It is also been found that very often the thermal stability and quenching speed of the quenching oil may be improved if in addition to the phenol-based detergent additive, a minor proportion by weight of an alkali metal or alkaline earth metal sulphonate is present. This sulphonate is preferably highly basic, and alkaline earth metal, (e.g. calcium) sulphonates of high basicity, e.g. having an alkalinity index of about 300 have been found to be particularly suitable.

The amount of sulphonate incorporated in the quenching liquid is preferably less than 20% by weight based on the total weight of quenching liquid and may be the same as that of the phenol-based detergent.

A minor proportion by weight based on the total weight of quenching liquid e.g. 0.005% by weight, of an antifoaming agent, for example a silicone, may be used.

Particularly suitable quenching oils have been found to be:

Hydrocarbon oil	Composition, wt./wt. percent	
	Phenol-based detergent additive	Sulphonate additive
85	15	
90	5	5
96	2	2

The invention is now described with reference to the following examples, in which the base hydrocarbon oil used was paraffinic distillate of medium viscosity having the following properties:

KV 210° F.	12.7
V.I.	100
Flash point ° C.	277

The phenol based detergent additive which was used in the examples was the reaction product obtained as follows; 14.5 wt. percent of a phosphosulphurised polybutene of molecular weight 750 to 900 having a sulphur content of 6.1 to 6.5 wt. percent and a phosphorus content of 3.2 to 3.7 wt. percent was mixed with 7.4 wt. percent of a mixture of C_7 to C_9 alkyl phenols in 46.7 wt. percent of a mineral hydrocarbon diluent oil. This mixture was purged with nitrogen from 90 to 130/133° C. and continued at a temperature of 127 to 135° C. 26.9 wt. percent of barium pentahydrate was added over 3 to 6 hours. Half an hour after the start of the barium pentahydrate addition carbon dioxide was blown in. The blowing in of CO_2 was continued for about half an hour after the last of the barium pentahydrate had been added and in all 4.5 wt. percent of CO_2 was added. Finally the reaction product was obtained by filtering.

The alkaline earth metal sulphonate detergent additive used in the examples was an overbased calcium sulphonate prepared as follows: Calcium carbide was added to methanol and carbon dioxide bubbled through. The reaction mixture thus obtained was added to the calcium salt of a polyalkylated benzene sulphonic acid, the calcium salt having MW of about 800, and the alkyl group being C_{12}. A complex was formed and this was treated with steam whereby the complex decomposed. The required overbased calcium sulphonate was obtained by filtering.

EXAMPLE I

In this example the quenching liquid consisted of 85% by weight of base hydrocarbon oil and 15% by weight of the phenol-based detergent additive. The path of quenching liquid was maintained at 200° C., and a ½" diameter B.S.En 31 steel bar (0.99 wt. percent C., 0.19 wt. percent Mn, 0.07 wt. percent Ni, 1.37 wt. percent Cr and Mb below 0.1 wt. percent) preheated to 810–830° C. was plunged into the bath. The mechanical properties of the steel after quenching were as follows:

Surface hardness ----------VPN--	840
Core hardness ----------VPN--	750

EXAMPLE II

The procedure of Example I was repeated except that the quenching liquid consisted of 90% by weight of base hydrocarbon oil, 5% by weight of the phenol-based detergent additive and 5% by weight of the overbased calcium sulphonate.

The mechanical properties of the steel after quenching were as follows:

Surface hardness ----------VPN--	800
Core hardness ----------VPN--	720

EXAMPLE III

The procedure of Example I was repeated except that the quenching liquid consisted of 96% by weight of base hydrocarbon oil, 2% by weight of the phenol-based detergent additive and 2% by weight of the overbased calcium sulphonate.

The mechanical properties of the steel after quenching were as follows:

Surface hardness ----------VPN--	840
Core hardness ----------VPN--	750

EXAMPLE IV

The procedure of Example I was repeated with a very critical 1¼" diameter SAE 8620 case hardened steel using

the same quenching liquid as in Example II. The core hardness was 300–390 VPN. The specification requirement (240–320 VPN) could not be achieved with other oils containing prior art quench speed improver, so that the quench oils of this invention showed great improvement.

EXAMPLE V

The process of Example I was repeated with a case-carburised 1½" diameter CM 60 bar using the same quenching liquid as in Example II. The core hardness was found to be 330 VPN.

EXAMPLE VI

The process of Example V was repeated using a case-carburised 1⅛" diameter SAE 8615 bar. The core hardness was found to be 281 VPN.

What is claimed is:

1. In a process for the quenching of a metal wherein said metal is first heated and its temperature is then lowered rapidly by immersion in a liquid quenching bath, whereby desired metallurgical changes are effected in said metal, the improvement which includes using as the quenching bath a liquid composition comprised of a major proportion of an oil having a flash point of at least 250° C., to which has been added from about 2 to about 15 weight percent, based on said composition, of a sulfur-containing derivative of an alkali metal salt or alkaline earth metal salt of an alkyl phenol compound having alkyl groups of from about 5 to 30 carbon atoms, said alkyl phenol compound being an alkylated phenol, an alkylated phenol thioether, or an alkylated thiophenol, said sulfur-containing derivative being further characterized in that it is the product of reaction of said alkali metal salt or alkaline earth metal salt with elemental sulfur or with a phosphosulfurized hydrocarbon of from 100 to 50,000 molecular weight.

2. Improvement as defined by claim **1** wherein said oil is a hydrocarbon oil.

3. Improvement as defined by claim **1** wherein said oil is a paraffinic distillate having a kinematic viscosity of from 9 to 14 at 210° F. and a viscosity index of from 80 to 105.

4. Improvement as defined by claim **1** wherein said phosphosulfurized hydrocarbon is phosphosulfurized polybutene.

5. Improvement as defined by claim **1** wherein said sulfur-containing derivative has associated therewith an alkali metal or alkaline earth metal carbonate.

6. Improvement as defined by claim **1** wherein said liquid composition also contains from about 2 to about 15 weight percent based on said composition, of an alkali metal or alkaline earth metal organic sulfonate.

7. Improvement as defined by claim **1** wherein said sulfur-containing derivative is the product of reacting phosphosulfurized polybutene with the barium salts of C_7 to C_9 alkyl phenols, said derivative including dispersed barium carbonate.

8. Improvement as defined by claim **1** wherein said liquid composition contains from about 2 to about 5 weight percent of an overbased alkaline earth metal salt of a polyalkylated benzene sulfonic acid.

9. Improvement as defined by claim **1** wherein said metal is carbon steel.

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