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(54) **QUENCHING FLUID COMPOSITION**

ABSCHRECKFLÜSSIGKEITZUSAMMENSETZUNG

COMPOSITION DE FLUIDE DE TREMPE

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(56) References cited:
GB-A- 984 723 **US-A- 1 742 791**
US-A- 1 976 210

- **BRENNAN R J ET AL: "A QUENCHANT BASED ON CANOLA OIL" ADVANCED MATERIALS & PROCESSES, AMERICA SOCIETY FOR METALS. METALS PARK, OHIO, US, vol. 152, no. 2, 1 August 1997 (1997-08-01), pages 32S-32U, XP000691682 ISSN: 0882-7958**
- **TOTTEN G E ET AL: "PERFORMANCE OF VEGETABLE OILS AS A COOLING MEDIUM IN COMPARISON TO STANDARD MINERAL OIL" JOURNAL OF MATERIALS ENGINEERING AND PERFORMANCE, ASM INTERNATIONAL, MATERIALS PARK, US, vol. 8, no. 4, August 1999 (1999-08), pages 409-416, XP000834238 ISSN: 1059-9495**
- **PRABHU K N ET AL: "METAL/QUENCHANT INTERFACIAL HEAT FLUX TRANSIENTS DURING QUENCHING IN CONVENTIONAL QUENCH MEDIA AND VEGETABLE OILS" JOURNAL OF MATERIALS ENGINEERING AND PERFORMANCE, ASM INTERNATIONAL, MATERIALS PARK, US, vol. 12, no. 1, February 2003 (2003-02), pages 48-55, XP001143507 ISSN: 1059-9495**

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Description

Technical field

[0001] The present invention relates to a new quench fluid composition used in the heat treatment of metals, comprising a mixture of vegetable oils and the use thereof.

State of the art

[0002] An appropriate quenching technique has always been an extremely important part of the heat treatment process of metals. Expensive, high value treated parts could result damaged if insufficient attention is paid to proper quenching procedure and means. The choice of the operative tempering conditions is therefore essential in view of the structural features and the technological aims which have to be reached.

[0003] Selection of a quenching agent is primarily governed by the processing specifications, the required physical properties, and the required microstructure.

Due to its versatile quenching performance, oil is the most widely used quenching medium, next only to water. The worldwide requirement for quenching oil today is estimated at between 50 million and 100 million gallons per year.

[0004] Among the various quenching media, oil continues to be favored because its quenching mechanism and cooling curves are well suited to the TTT (time, temperature, and transformation) and CCT (continuous cooling transformation) diagrams of many types of steel.

[0005] Quenching of steel in liquid medium consists of three distinct stages of cooling: the vapor phase, nucleate boiling, and the convective stage. In the first stage, a vapor blanket is formed immediately upon quenching. This blanket has an insulating effect, and heat transfer in this stage is slow since it is mostly through radiation. As the temperature drops, the vapor blanket becomes unstable and collapses, initiating the nucleate boiling stage.

[0006] Heat removal is the fastest in this stage, due to the heat of vaporization, and continues until the surface temperature drops below the boiling point of the quenching medium. Further cooling takes place mostly through convection and some conduction.

[0007] During the quenching process, there are two sorts of stresses involved: thermal stresses due to rapid cooling, and transformation stresses due to the increase in volume from austenite to martensite microstructure. Those stresses can cause excessive distortion or even cracks.

[0008] However, oil has a unique desirable cooling response in minimizing those effects. Consequently, oil will continue to be used for quenching as long as it is affordable.

[0009] For the application in heat baths there are several types of quenching oils suitable for steels with low to high hardenability. Thanks to the properties of these oils, it is possible to quench also into the martensitic temperature range - i.e. in a range between 160 and 250°C - with minimum distortion, while still obtaining the desired properties in metal parts.

[0010] Besides hardenability, selection of an oil formulation depends on part geometry and thickness, and the degree of distortion that can be tolerated. For example, hot oil is required for smaller parts with high hardenability to achieve the desired mechanical properties with minimum distortion.

[0011] Quenching oils are available with flash points ranging from 130°C to 290°C. The operating temperature of the oil in an open quench tank is normally at least 65°C below its flash point. When the quench tank is operated under a protective atmosphere, oil can be used at as high as 10°C below the flash point. The operating range of a heat bath quenching oils is normally from 10°C to 230°C.

A lower operating temperature is in any case helpful in minimizing thermal degradation of the oil.

[0012] Originally, oil was used without any additives. It was slow in cooling and susceptible to oxidation. Research was carried out to overcome these shortcomings by adding certain chemical additives to the oil. In addition, the objective was to make oil quenching more reliable and uniform, and to control the vapor phase by starting the nucleate boiling stage sooner. Consequently, the term "fast oil" is applied to oil with such additives. Some oils also have additives that extend the nucleate boiling stage to achieve deeper hardening for some steel. Specially formulated oils also are available for vacuum heat-treating operations.

[0013] The use of mineral oils mixtures for quenching purposes is described for instance in the patents US 3 853 638, US 4 465 523 and US 6 239 082.

Those patents disclose different compositions for quenching processes comprising mineral oils and additive substances which should achieve the stabilization of the chemical and technological properties of the mixtures.

[0014] Although the benefits of using mineral oils are great, there are many concerns to be addressed to their use, specifically, safety, disposal, and availability.

[0015] Safety risks, which are due to the inflammability of those oils, and the strictly connected toxicological aspect, depends on the chemical nature of the mineral oils, which in the most cases are Hydrocarbons derivatives. This involves the risk of formation of oxidation compounds with a subsequent waste disposal difficulty.

[0016] Furthermore, the operating conditions are also characterized by health affecting additives used in the oil mixture to optimize and stabilize at the same time the fast cooling process at high temperatures.

[0017] In the most cases those additives have a high toxicity degree - like many compounds belonging to the petroleum sulfonates and to the sulfurate class, largely used in mineral oils tempering mixtures - thus compromising the general environmental security. In addition, this aspect involves a biodegradability problem of the used oils, which depends directly on the already cited aspect of the waste disposal.

[0018] Another factor which derives from the process itself and which involves not only the empirical aspect of the procedure but also the economical one is the low recovery obtained with mineral oils, since not all the mixture used can be employed for subsequent uses, with the consequent loss of material. In fact, for especially large quenching operations, systems are able to maximize recovery from about 60 to 80% of the oil used. This is due to the thermal degradation and chemical degeneration of paraffinic and olefinic components and it represents a negative aspect of the technique which is still difficult to overcome.

Scope of the invention

[0019] Scope of the present invention is therefore to provide a fluid composition for quenching processes with a low toxicological impact.

Another object of the invention is also a tempering fluid composition with a good stability and biodegradability.

A further object of the invention is to provide a fluid quenching composition which allows to achieve a high recovery of both tempering material and tempered metal after every use.

Description of the invention

[0020] A solution to the above cited problems is given by the subject matter of claim 1.

[0021] The quenching fluid composition according to the present invention comprises:

- from 65 to 85% w/w of oleic acid
- from 6 to 10% w/w of linoleic acid
- from 4 to 15% w/w of stearic acid and
- from 4 to 10% w/w of palmitic acid
- 1% w/w of a mixture comprising Myristic, Palmitoleic, Margarinic, Margaroleic, α-Linoleic, Arachidic, Eicosenoic Behenic and Erucic acid.

[0022] This composition does not involve the use of mineral oils, so that all the cited problems strictly related to their use have been avoided.

[0023] The oil composition described above is obtained by the extraction from hazelnuts, sunflower seeds, Brassica napus (rapeseed) and soybeans. By comprising essentially vegetable oils, the object of the present invention is then particularly suited as quenching fluid composition with low environmental impact and is also characterized by a high biodegradability and practically no toxicity.

[0024] Another important property of the disclosed mixture is that the composition results transparent and clear, thus avoiding the formation of the "ash of deposit" always leaved behind on the metal after the immersion in mineral oil baths. This layer not only affects the brightness and the cleanliness of the metal surface but is also difficult to be removed from the metal surface.

[0025] The use of a vegetal composition further allows to simplify the removal of the bath from the metal parts, an operation which in the present case can be done without the necessity of using extra-washing methods after the heat treatment.

[0026] In order to avoid the thermal degradation and the degeneration of the oils at the working temperatures, what compromises the quality and the "duration" of the mixture, different stabilizing additives are used.

Those additives are chosen among the group consisting of Octyl-Butyl Diphenylamine, long-chain sulphonate acid salts, phenols derivatives and Benzotriazoles like the N,N-bis(2-ethylesyl)-4-metyl-1H-benzotriazole-1-metylamine and the N, N-bis(2-ethylesyl)-5-metyl-1H-benzotriazole-1-methylamine.

[0027] They are intended to stabilize the composition without compromising the chemical and physical characteristics of the oil mixture and in conformity with the main properties of the fluid, i.e. the biodegradability and the low toxicological impact.

[0028] Since the present fluid quenching composition derives from oil extractions performed on natural products, it has undoubtedly better application qualities than the quenching compositions constituted of mineral oils of the prior art.

[0029] A first advantageous aspect is linked to the vast disposal offered by the natural origin of the oils and also to the low costs involved for their preparation. This grants a large source of prime materials which does not apply in the

case of mineral oils and which is strictly correlated to initial substances which are extremely easy to obtain and to be treated.

[0030] Furthermore, by limiting the thermal degradation and by adding stabilizing compounds, the fluid offers a recovery next to the 99% value as regards the oil reclaiming and the tempering technological effect on metals.

[0031] In fact, the bath can be reutilized, lowering in this way the environmental costs and extending the "life time" of the quenching composition and it avoids completely the risks of material deformations.

Examples of application

[0032] The following example has a pure explanatory nature and should be therefore interpreted without any restriction to the general inventive concept of the present invention.

[0033] The quenching fluid formulation of the present invention has been used in tempering processes at different temperatures both in covered and opened tank bath.

[0034] The obtained results are summarized in table 1:

	30°C		60°C		80°C		100°C	
°C	s	°C/s	s	°C/s	s	°C/s	s	°C/s
600	4.0	76.5	3.8	82.5	3.8	77.8	3.8	74.5
500	5.6	48.2	5.4	50.9	5.4	47.6	5.4	44.8
400	8.4	24.8	8.0	26.6	8.2	23.5	8.8	19.3
300	15.0	8.9	13.6	10.3	16.0	6.6	20.0	5.0
200	34.6	3.3	35.4	2.8	41.2	2.5	48.8	1.9
	Max. vel. 94°C/s at 699°C		Max. vel. 103°C/s at 713°C		Max. vel. 100°C/s at 702°C		Max. vel. 100°C/s at 721°C	

[0035] The previous table shows that the fluid can be used at the different temperatures by maintaining in any case versatility and stability at the different operating conditions.

[0036] The composition is preferably employed at a temperature of 60°C, at which the best results have been observed.

[0037] Under those conditions, analytical and physical-chemical analyses have been performed, giving the following results:

Aspect:	clear
Color:	L2
Density:	0.9147
cSt 40°C	40.7
cSt 100°C	8.8
V.I.	204
Inflammability P.M.:	225
Inflammability C.O.C.:	290
Acidity N.N.:	0.9
Carbon rest:	0.41%
Ashes:	0.07%
Sliding index:	-21°C

[0038] An oxidation test at the "thermal shock" has been also conducted and the obtained results reflect the stability and the reliability of the mixture:

- viscosity increase from 40.7 to 69.5
- increase of carbon rest from 0.41 to 0.74
- constant inflammability
- evaporation loss of 1%
- no deposits on the metal surface.

Claims

1. Vegetable quenching fluid composition comprising:

   - from 65 to 85% w/w of oleic acid
   - from 6 to 10% w/w of linoleic acid
   - from 4 to 15% w/w of stearic acid and
   - from 4 to 10% w/w of palmitic acid
   - 1% w/w of a mixture comprising Myristic, Palmitoleic, Margarinic, Margaroleic, α-Linoleic, Arachidic, Eicosenoic Behenic and Erucic acid.

2. Quenching fluid composition according to claim 1, **characterised in that** such composition is obtainable by the extraction from hazelnuts, sunflower seeds, *Brassica Napus* and soybeans.

3. Composition according to claim 1 or 2, **characterized by** the presence of stabilizing additives.

4. Composition according to claim 3,
   characterized in that the additives are chosen among the group consisting of Octyl-Butyl Diphenylamine, long-chain sulphonate acid salts, phenols derivatives and Benzotriazoles like the N,N-bis(2-ethylesyl)-4-metyl-1H-benzotriazole-1-metylamine and the N,N-bis(2-ethylesyl)-5-metyl-1H-benzotriazole-1-methylamine.

5. Use of a composition according to the claims 1 to 4 as quenching bath for metals.

Patentansprüche

1. Pflanzliche Abschreckungsflüssigkeitszusammensetzung, umfassend:

   - zwischen 65 und 85 Gew.-% Ölsäure
   - zwischen 6 und 10 Gew.-% Linolsäure
   - zwischen 4 und 15 Gew.-% Stearinsäure und
   - zwischen 4 und 10 Gew.-% Palmitinsäure
   - 1 Gew.-% einer Mischung, umfassend Myristin-, Palmitolein-, Margarin-, Margarolein-, α-Linol-, Arachin-, Eicosen-, Behen- und Erucasäure.

2. Abschreckungsflüssigkeitszusammensetzung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** eine derartige Zusammensetzung durch Extraktion aus Haselnüssen, Sonnenblumenkernen, *Brassica Napus* und Sojabohnen erhältlich ist.

3. Zusammensetzung gemäß Anspruch 1 oder 2, **gekennzeichnet durch** die Gegenwart von Stabilisierungszusätzen.

4. Zusammensetzung gemäß Anspruch 3, **dadurch gekennzeichnet, dass** die Additive ausgewählt werden aus der Gruppe bestehend aus Octyl-butyl-diphenylamin, langkettigen Sulfonat-Säuresalzen, Phenolderivaten und Benzotriazolen wie N,N-Bis-(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamin und N,N-Bis-(2-ethylhexyl)-5-methyl-1H-benzotriazol-1-methylamin.

5. Verwendung einer Zusammensetzung gemäß den Ansprüchen 1 bis 4 als Abschreckungsbad für Metalle.

Revendications

1. Composition végétale de fluide de trempe comprenant :

   - entre 65 et 85 % masse pour masse d'acide oléique,
   - entre 6 et 10 % masse pour masse d'acide linoléique,
   - entre 6 et 15 % masse pour masse d'acide stéarique et
   - entre 4 et 10 % masse pour masse d'acide palmitique,
   - 1% masse pour masse d'une mélange d'acide myristique, palmitoléique, margarinique, margaroléique, α -

linoléique, arachidique, eicosénoique, béhénique et érucique.

2. Composition végétale de fluide de trempe selon la revendication 1, **caractérisée en qu'**on peut obtenir une telle composition en réalisant une extraction de noisettes, de graines de tournesol, de *Brasica Napus* et de fèves de soja.

3. Composition selon la revendication 1 ou 2, **caractérisée par** une présence d'additifs stabilisants.

4. Composition selon la revendication 3, **caractérisé en ce que** les additifs sont choisis parmi le groupe composé de octyle - butyle - diphénylamine, de sels de l'acide sulfurique à longue chaîne, des dérivés de phénol et des benzotriazoles comme le N, N - bis (2 - éthylhexyle) - 4 - méthyle - 1H - benzotriazole - 1 - méthylamine et le N, N - bis (2 - éthylhexyle) - 5 - méthyle - 1H - benzotriazole - 1 - méthylamine.

5. Utilisation d'une composition selon les revendications 1 à 4 en tant que bain de trempe pour des métaux.