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CONTINUOUS CASTING PROCESS

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ABSTRACT OF THE DISCLOSURE

A composition is prepared suitable for lubricating the interface of liquid metal and mold during the continuous casting of metals. This lubricating composition contains an aliphatic or aromatic carboxylic acid having 2 to about 40 carbon atoms, e.g., the acids obtained by hydrolysis of and contained in Crambe and rapeseed oils and mixtures of them, and a mineral lubricating oil having a low carbon residue and low aromatic carbon content which can be prepared by a two-stage catalytic hydrogenation process.

This invention is concerned with a lubricating composition suitable for use in the continuous casting of metals. More specifically, this invention is concerned with a product useful for lubricating the metal-mold interface during the continuous casting of metals, which composition contains a carboxylic acid and a mineral lubricating oil component low in carbon residue and aromatic carbon content. The mineral lubricating oil can be made by a two-stage catalytic hydrogenation process.

In the continuous casting of metals, molten metal is cast directly and continuously into billets and slabs without the necessity for the usual pouring into ingots, cooling, reheating and rolling normally required in other processes. The machinery employed in the continuous casting process may be of a number of designs but all contain certain basic elements. These are, in the order in which they are employed in the operation, the ladle, the tundish, the mold where primary cooling takes place, a secondary cooling section, withdrawal rolls and cut-off equipment. In a typical casting operation molten metal, e.g., steel, is poured from the ladle into the tundish. From the tundish the liquid metal flows in a continuous, uniform stream into the mold, which is equipped with a cooling system employing, for example, water as the coolant. It is in this mold that partial solidification of the steel first takes place. Normally a "tube" or billet of metal is formed consisting of a cooled, solid outer layer of metal surrounding a molten inner core of metal. This billet passes continuously from the mold, through withdrawal rollers and is further cooled for example by spraying with water prior to passing through the cut-off equipment where the billet is cut by torches or by hydraulic knives into the desired lengths.

One of the most significant problems which has been encountered in the continuous casting of metals, particularly steel, is that of providing satisfactory lubrication at the mold metal interface. The lubricant employed must, first be all, prevent welding of the steel to the mold surface. Further, the lubricant should be consumed in combustion when it contacts the high temperature liquid metal (e.g., about 2800° F. for molten steel) with little or no residue left. Residue from the combustion of the lubricant may become entrained in the steel and result in "blow outs." Finally, as the lubricant is consumed, there should be a minimum of smoke since smoke prevents visual observation of the steel-mold interface which is necessary to proper control of the lubricant flow rate. The smoke is also objectionable to the operating personnel.

Various compositions have in the past been employed as lubricants for continuous metal casting processes. Early processes employed used transformer oil, which, though inexpensive, contained debris which caused "blow outs" in the steel and, through failure to provide adequate lubrication, permitted welding to take place between the steel and the mold. More recently rapeseed and Crambe oils have been extensively employed in these processes as lubricants. These oils are, however, rather expensive and produce an unacceptable amount of smoke.

Now in accordance with this invention, it has been found that the interface formed between the metal and the mold during the continuous casting of metals can be effectively lubricated without the production of excessive smoke or residue, by using a lubricating composition comprising a base or major amount of a mineral oil of lubricating viscosity having a low carbon residue and a low aromatic carbon content, and a minor amount, e.g., about .01 to 45 preferably about 0.1 to 20, weight percent of a mineral oil-soluble, aromatic or aliphatic hydrocarbon carboxylic acid having 2 to about 40, preferably about 12 to 32 carbon atoms and one or more carboxylic acid group. Preferably the acid has at least about 6 carbon atoms, e.g. the fatty acids of 12 to 22 carbon atoms, either saturated or unsaturated, such as stearic, hexoic, octanoic, oleic, linoleic, linolenic and alkylated benzoic acids. Also dimers of these unsaturated acids can be used as can the acids obtained by hydrolysis and contained in Crambe and rapeseed oils. Oleic acid is particularly preferred.

Tables A and B show respectively the analysis of acids obtained by hydrolysis and contained in Crambe and rapeseed oils.

TABLE A.—GAS-LIQUID PARTITION CHROMATOGRAPHIC ANALYSIS OF CRAMBE OIL

Ret. time, min.	Peak No.	Component	Percent
4.05	1	Myristic	.02
6.50	2	Palmitic	1.62
7.74	3	Palmitoleic	.11
10.6	4	Stearic	.64
12.7	5	Oleic	14.53
15.6	6	Linoleic	6.60
17.5	7	Arachidic	.78
20.5	8	Linolenic	9.18
26.0	9	C-20(−4H)	.18
29.2	10	Behenic	2.51
35.2	11	Erucic	60.22
42.4	12	C-22(−4H)	1.02
42.8	13	Lignoleric	.59
55.3	14	C-24(−4H)	2.02
Total			100.02

Sap. No.	173
I_2 No.	90–96
Titer	-----
Unsaponifiables	0.6
Density	.9408
Ref. Index	1.4719
M.P.	6° C.
Ash	.02
FFA	L 1

TABLE B.—GAS-LIQUID PARTITION CHROMATOGRAPHIC ANALYSIS OF RAPESEED OIL

Peak No.	Component	Percent
1	Lauric	.11
2	Myristic	.09
3	Palmitic	3.57
4	Palmitoleic	.21
5	Stearic	1.27
6	Oleic	14.21
7	Linoleic	14.24
8	Arachidic	1.36
9	Linolenic	14.48
10	Gadoleic	.69
11	Erucic	49.75
	Total	99.98

Sap. No.	170–180
I_2 No.	97–112
Titer	11.5–15° C.
Ash	.02
Unsaponifiables	1% Max.
FFA	1% Max.
Sp. grav.	.910–.916

Rather than use the carboxylic acids as such, their oil-soluble esters can be employed in the compositions of this invention. The esters can be those of monohydric or polyhydric alcohols, e.g. glycerides, and often the alcohol group will be aliphatic, including cycloaliphatic, and contain up to about 24 carbon atoms. The alcohol group can be saturated or unsaturated as in the case of sperm oil. Thus, the suitable alcohols include glycerol, methanol, lauryl alcohol, oleyl alcohol, etc.

The mineral oil employed in the compositions of this invention is of lubricating viscosity and has a carbon residue below about 0.1, or even below about 0.05, Ramsbottom (ASTM D–524), and less than about 1 percent aromatic carbon atoms (carbon type analysis), preferably essentially none. Although the mineral oil can be derived from various crudes, there is a preference to use a mixed base oil rather than a naphthenic oil as the source of the lubricating oil component of the product. Mixed base crudes, and paraffinic crudes as well, can more readily yield predominantly paraffinic lubricating oil fractions, and it is preferred that the oil component of the compositions have at least about 60 percent paraffinc carbon atoms.

The viscosity of the lubricating oil component of the compositions of this invention is such that upon mixture with the carboxylic acid the formulation is fluid and readily handled as by pumping. Generally, the lubricating oil component, which can if desired be a mixture of oils, has a viscosity of at least about 100 SUS at 100° F. and often the viscosity does not excees about 4000 SUS at 100° F. The choice of oil can depend on the type of metal being cast or the quality desired in the cast product. Thus with forging grade steel the oil can with advantage have a flash point of at least about 500° F. while with lower grade products, such as non-forging steel, lower flash point oils of the order of at least about 280° F., preferably at least about 290° F., can be employed with acceptable results.

The mineral oil employed in the present invention can be prepared by hydrogenating a distillate mineral lubricating oil feedstock in a dual stage catalytic system. In the first stage of the process the raw oil is contacted with hydrogen at elevated temperature in the presence of a sulfur-resistant hydrogenation catalyst. The hydrogenated oil from the first stage is then subjected to a second hydrogenation operation which involves contact with hydrogen in the presence of a platinum group metal-promoted hydrogenation catalyst, usually under less severe reaction conditions than used in the first hydrogenation stage, to produce the high quality mineral oil.

This process has been found to be particularly effective in providing mineral oils of high quality and in high yields, e.g., greater than about 90%. The oil feedstocks often have a viscosity in the range of about 50 to 7500 SUS at 100° F. If the oils contain wax, and a product of low pour point is desired, the oils are dewaxed, preferably prior to the first hydrogenation operation, although the dewaxing can follow the first hydrogenation stage. Dewaxing can be carried out, for example, by using a solvent such as methylethyl ketone and toluene to obtain an oil with a pour point (ASTM D–97) below about 25° F. The pour point necessary after dewaxing is determined by that required in the finished oil.

The treatment in the first hydrogenation stage can be conducted at temperatures of about 600 to 750° F. Other suitable reaction conditions include pressures of about 1500 to 5000 p.s.i.g., weight hourly space velocities (WHSV) of about 0.1 to 1, and a hydrogen rate of about 1000 to 5000 s.c.f./b. Preferred operating conditions are temperatures of about 600 to 700° F., about 1500 to 3000 p.s.i.g. pressure, a WHSV of about 0.2 to 0.5, and hydrogen flow rate of about 1000 to 3000 s.c.f./b.

The hydrogenated oil from the first hydrorefining stage can then be subjected to hydrogenation over a platinum metal catalyst at temperatures of about 450 to 700° F. Other suitable reaction conditions include pressures of about 1000 to 5000 p.s.i.g., WHSV of about 0.15 to 1, and a hydrogen feed rate of about 500 to 5000 s.c.f./b. To provide less severe reaction conditions in the second hydrogenation stage the average temperature is often at least about 50° F., preferably at least about 75° F., less than that of the first hydrogenation stage. The preferred range of conditions for the second stage are temperatures of about 525 to 650° F., pressures of about 1000 to 3000 p.s.i.g., WHSV of about 0.25 to 0.5, and hydrogen flow rates of about 500 to 3000 s.c.f./b.

The catalyst of the first hydrogenation operation can be of any of the sulfur-resistant, non-precious metal hydrogenation catalysts, some of which are conventionally employed in the hydrogenation of heavy petroleum oils. Examples of suitable catalytic ingredients are tin, vanadium, members of Group VI–B in the Periodic Table, i.e., chromium, molybdenum and tungsten, and metals of the iron group, i.e., iron, cobalt and nickel. These metals are present in catalytically effective amounts, for instance, about 2 to 30 weight percent and may be present in the form of oxides, sulfides, or other form. Mixtures of these materials can be employed, for example, mixtures or compounds of the iron group, metal oxides or sulfides with the oxides or sulfides of Group VI–B constitute very satisfactory catalysts. Examples of such mixtures or compounds are nickel molybdate, tungstate, or chromate (or thiomolybdate, thiotungstate or thiochromate) or mixtures of nickel or cobalt oxides with molybdenum, tungsten or chromium oxides. As the art is aware, these catalytic ingredients are generally employed while disposed on a suitable carrier of the solid oxide refractory type, e.g., a predominantly calcined or activated alumina. Commonly employed catalysts have about 1 to 10% of an iron group metal and 5 to 25% of a Group VI–B metal (calcined as the oxide). Advantageously, the catalyst is cobalt molybdate or nickel molybdate supported on alumina. Such preferred catalysts can be prepared by the method described in U.S. Pat. 2,938,002.

As aforementioned, the catalyst of the second hydrogenation operation of the present invention is a platinum group metal-promoted catalyst. This catalyst is to be distinguished from the catalysts of the first hydrogenation in that it is not normally considered to be sulfur-resistant. The catalyst includes catalytically effective amounts of the platinum group metals of Group VIII, for instance platinum, palladium, rhodium or iridium, which are present in catalytically effective amounts, generally in the range of about 0.01 to 2 weight percent, preferably about 0.1 to 1 weight percent. The platinum group metal may be present in the metallic form or as a sulfide, oxide or other combined form. The metal may interact with other constituents of the catalyst but if during use the platinum group metal is present in metallic form, then it is pre-

ferred that it be so finely divided that it is not detectable by X-ray diffraction means, i.e., that it exists as crystallites of less than about 50 A. size. Of the platinum group metals, platinum is preferred. If desired, the catalysts of the first and second hydrogenations can be hydrogen purged or prereduced prior to use by heating in the presence of hydrogen, generally at temperatures of about 300 to 600° F. for purging or at about 600 to 800° F. for prereduction.

Although various solid refractory type carriers known in the art may be utilized as a support for the platinum group metal, the preferred support is composed predominantly of alumina of the activated or calcined type. The alumina base is usually the major component of the catalyst, generally constituting at least about 75 weight percent on the basis of the catalyst and preferably at least about 85 to 99.8 percent. The alumina catalyst base can be an activated or gamma-family alumina which can be derived from alumina monohydrate, alumina trihydrate, amorphous hydrous alumina or their mixtures. A catalyst base precursor which can be used is a mixture predominating in, or containing a major proportion of, for instance about 65 to 95 weight percent, of one or more of the alumina trihydrates, bayerite I, nordstrandite or gibbsonite, and about 5 to 35 weight percent of alumina monohydrate (boehmite amorphous hydrous alumina or their mixtures). The alumina base can contain small amounts of other solid oxides such as silica, magnesia, natural or activated clays (such as kaolinite, montmorillonite, halloysite, etc.), titania, zirconia, etc., or their mixtures.

Following either of the hydrogenation operations of the present invention the hydrogenated oils in each case can be distilled or topped to remove any hydrocracked or other light materials that may have been formed. The removal of light products increases the flash point of the oil. The degree of topping desired will depend on the particular lubricating oil fraction being hydrogenated, the particular hydrogenation conditions employed and the flash point desired for the product. Thus, the amount of topped overhead that may be taken off in the topping or distillation step after either hydrogenation operation may often vary from about 0 to 50% with 0 to 10% being preferred.

In order to obtain effective lubrication during the continuous casting of metal and to prevent the metal from welding to the mold, a continuous film of lubricant is provided to the steel-mold interface. Typically, in machinery now being used for continuous casting, a pump is provided which regulates the amount of lubricant present. The amount of lubricant provided as well as the effectiveness of its distribution over the mold surface is of importance. Too little lubricant in a particular spot may result in welding; too much lubricant causes sputtering which occurs when excessive lubricant in the steel-mold interface suddenly and violently vaporizes. Liquid steel blown from the mold during the eruption is a hazard to operating personnel. Effective lubricant distribution in machines now in use is provided often by small slits or orifices in the side of the mold. Additionally, it has been found effective to have the lubricant pumped into reservoirs so located that the lubricant spills over out of the reservoirs evenly onto the mold walls. The lubricating process of the present invention, employing the lubricating compositions which have been described can be carried out using the various procedures and equipment known in the art for supplying lubricant to the continuous casting mold.

The following description is typical of the procedures which can be employed in the process of the present invention. Steel is heated in an electric furnace and transferred to a ladle. The ladle is placed in a rack over a "T" shaped tundish. A valve in bottom of ladle is controlled by the operator who observes the liquid steel level in tundish. The tundish contains several holes through which steel flows to casting chutes. Each hole is equipped with a valve which is opened and closed by the operator.

Beneath the tundish is positioned a block containing the casting positions, each consisting of a cylindrical block equipped with a water cooling system. The cylindrical blocks are oscillated up and down during the pour. In the center of the cylindrical block is a square hole in which the copper casting chute or mold is placed. The chute is tightly sealed to the block and cooling water is circulated around it. As the cylindrical block oscillates up and down, the chute also oscillates.

The pour is started by filling the tundish with steel from the ladle. Steel flows out of the tundish in a rod shape, and falls a short distance through air before entering the casting chute. Before starting the pour, a pyramid-shaped block is inserted in the lower end of the casting chute. Steel freezes to this block, and the weight of steel eventually forces the block out of the casting chute. The block is fastened to a guiding chain and this device is used to thread the formed billet through guideposts on a lower horizontal ramp. The weight of liquid steel being continuously added at top of chute forces partially solidified steel out the bottom of chute. The cooling which takes place in the chute forms a solid outer layer around inner core of the liquid steel. On leaving chute, the billet is bent from the vertical to the horizontal position. The continuous billet is passed through a water spray zone and cut into lengths suitable for loading.

In one machine employed, lubricant is pumped from central lube system through tubing to the top of the casting chute. Lubrication inlets were provided on facing sides of the chute. In another machine, lubricant is pumped into four reservoirs and the lubricant overflowed evenly to lubricate the mold. One reservoir was associated with each wall of the mold. Lubricant flowed down the sides of the chute, and burst into flames when the steel was contacted. Some of lubricant danced over the liquid steel surface (2800° F.) like water on a hot pancake griddle. Eventually a dancing ball of lubricant struck and wet the cooler copper mold. The lubricant was completely consumed in a single pass through the machine while the wetting action provided lubrication.

The preparation of a petroleum lubricating oil which is useful in the present invention is illustrated by the following example.

EXAMPLE

The starting material is a raw lubricating oil distillate fraction obtained by vacuum distillation of a Gulf Coast, naphthenic base, reduced crude oil, the raw distillate having a viscosity of 1000 SUS at 100° F. and a pour point of about −5° F. This oil is hydrogenated at 2500 p.s.i.g. hydrogen partial pressure, 680° F., 0.25 weight hourly space velocity, and a hydrogen rate of 2200 standard cubic feet of hydrogen per barrel of oil over a cobalt molybdate on alumina catalyst containing 2.7% CoO and 11.9% MoO_3.

The hydrogenated product is flashed to remove hydrogen and stripped to remove essentially all materials lighter than lubricating oil. The stripped product is dried and then subjected to a second hydrogenation operation at a pressure of 2500 p.s.i.g. hydrogen partial pressure, a temperature of 575° F., a weight hourly space velocity of 0.25 and a hydrogen rate of 2500 standard cubic feet of hydrogen per barrel of feed over a platinum on alumina catalyst containing 0.6% platinum. This material is then flashed to remove hydrogen and the oil stripped to remove materials boiling below the desired product.

The properties of three products made by dual hydrogenation are listed in Table I. The feedstocks which were hydrogenated to give oils 1 and 2 of Table I were derived from naphthenic base crude oils, oil 2 being a typical product made by Example I above. The feedstock which gave oil 1 would typically have a viscosity of about 140 SUS at 100° F. A feedstock which can be used to produce

oil 3 of Table I can be derived from a mixed base crude oil and can be a dewaxed raffinate from the phenol treatment of the row distillate, the dewaxed product having a viscosity of about 230 SUS at 100° F.

TABLE I

Products	1	2	3
Gravity, ° API	26.9	23.0	33.0
Flash, ° F	315	390	385
Viscosity, SUS at 100° F	95.45	582.8	164.8
Viscosity, SUS at 210° F	37.74	55.23	43.78
Pour, ° F	−55	−15	15
Color, Saybolt	+30	+25	+30
Molecular weight	333	416	487
Viscosity-gravity constant	0.825	0.828	0.800
Specific dispersion	100.0	101.8	100.1
Carbon residue, Ramsbotton (carbon type)	0.01	0.05	0.01
Hydrocarbon analysis, percent:			
Aromatic carbons	0	0	0
Naphthenic carbons	58	57	31
Paraffinic carbons	42	43	69
Clay-gel analysis, percent:			
Resins	0	0	0
Non-resinous aromatics	0.1	8.0	0
Saturates	99.9	92.0	100

The following formulation is typical of the lubricating composition of the present invention:

TABLE II

Composition:	A
Oil 1, Table 1, wt. percent	65.6
Oil 2, Table 1, wt. percent	24.4
Oleic acid, wt. percent	10.0

Tests on blended product A were made with the following results:

TABLE III

Test data on continuous casting oil

Gravity ° API	25.8
Viscosity at 100° F. cs.	26.97
Viscosity SUS	128.0
Viscosity at 210° F. cs.	4.304
Viscosity SUS	40.40
Viscosity index	51
Flash ° F.	340
Fire ° F.	370
Pour ° F.	−35
Iodine No.	9.3
Refractive index 20° C.	1.4839
Carbon residue, percent	0.060
Color, ASTM	L2

Product A was evaluated in a commercial continuous steel (non-forging) casting operation. The mold size was 4½" x 4¼". In testing product A, it was applied to the mold by machine at the rate of 0.035 gal./ton of steel, as well as applied by hand spraying. The results of the tests were as follows:

Product:	A
Smoke	Pass
Duration of lubrication,[1] seconds	20
Travel Test [2]	Pass

[1] Time each application of product gave satisfactory lubrication at steel-mold interface, 15 seconds is borderline; 20 seconds is a solid pass.

[2] Measure of the ability of the lubricant to travel around the steel-mold interface.

Excellent performance was obtained and after 12 pours (144 tons of steel) the product A was still performing satisfactorily at the reduced rate of consumption.

It is claimed:

1. A method of lubricating the metal-mold interface in the continuous casting of metals which method comprises providing a non-aqueous, fluid lubricating composition to said metal-mold interface, said non-aqueous, fluid lubricating composition consisting essentially of a major amount of a mineral oil of lubricating viscosity and having a carbon residue below about 0.1% (Ramsbottom) and an aromatic carbon content less than about 1%, and a minor weight percent in the range of about 0.01 to 45 weight percent of oil-soluble fatty acid of about 12 to 22 carbon atoms or an oil-soluble ester thereof.

2. The method of claim 1 wherein the metal is steel.

3. The method of claim 1 wherein the hydrocarbon oil present in the non-aqueous lubricating composition has a viscosity of at least about 100 SUS at 100° F. and contains less than about 60 percent paraffinic carbon atoms.

4. The method of claim 3 wherein the metal is steel.

5. The method of claim 1 wherein the lubricating oil present in the non-aqueous lubricating composition is prepared by hydrogenating a distillate mineral lubricating oil feedstock in a dual catalytic stage system, the first stage of which employs a sulfur-resistant hydrogenation catalyst at temperatures of about 600 to 750° F. and the second stage of which employs a platinum group metal catalyst at temperatures of about 450 to 700° F.

6. The method of claim 5 wherein the metal is steel.

7. The method of claim 5 wherein in preparing the lubricating oil by hydrogenation the first stage catalyst is nickel or cobalt and molybdenum supported on alumina and the second stage catalyst is platinum-alumina.

8. The method of claim 7 wherein the metal is steel.

9. The method of claim 1 wherein about 0.1 to 20 weight percent of fatty acid or ester thereof is present in the non-aqueous lubricating composition.

10. The method of claim 9 wherein the fatty acid present in the non-aqueous lubricating composition is oleic acid.

11. The method of claim 10 wherein the metal is steel.

12. The method of claim 9 wherein the metal is steel.

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