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[54] **LUBRICATNG COMPOSITION AND METHOD FOR TREATING METAL-MOLD INTERFACE IN CONTINUOUS CASTING OPERATION**

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[56] **References Cited**

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[57] **ABSTRACT**

A lubricating composition is prepared suitable for lubricating the interface of liquid metal and mold during the continuous casting of metals. This lubricating composition contains both the dimer and trimer of an unsaturated fatty acid, a glyceride oil, e.g., triglyceride, as a solubilizing agent, 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.

16 Claims, No Drawings

LUBRICATNG COMPOSITION AND METHOD FOR TREATING METAL-MOLD INTERFACE IN CONTINUOUS CASTING OPERATION

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 composition useful for lubricating the metal-mold interface during the continuous casting of metals, which composition contains both dimer and trimer of an unsaturated fatty acid, a glyceride oil, especially a triglyceride, as a solubilizing agent, and a mineral lubricating oil component low in carbon residue and aromatic carbon content. The mineral lubricating oil can be made by a two-state 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 cutoff 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 cutoff 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-liquid metal interface. The lubricant employed must, first of all, prevent welding of the steel to the mold surface. Further, the lubricant should be consumed in combination when it contacts the high-temperature liquid metal (e.g., about 2,800° 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 out." 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 can be employed as lubricants for continuous metal casting processes. One such lubricant contains a dimer of an unsaturated fatty acid and a mineral lubricating oil of low carbon residue and low aromatic carbon content.

In formulating this product it is desired to employ the dimer acid in its less expensive commercially available form in which the dimer is mixed with trimer of the unsaturated fatty acid. Unfortunately the use of the mixed dimer-trimer acids in the base mineral oil is unsatisfactory since insolubles appear in the product.

Now in accordance with the present invention, it has been found that the provision of a glyceride oil, especially triglyceride oil, in the mineral oil-dimer-trimer acid mixture overcomes the foregoing described insolubles problem, and at the same time a product is formed which serves as an effective lubricant at the interface formed between the metal and the mold during the continuous casting of metals without the production of excessive smoke or residue. The lubricating composition of this invention thus comprises a major amount of mineral oil of lubricating viscosity having a low carbon residue and a low aromatic carbon content, about 2 to 15, preferably about 3 to 10, weight percent of total dimer and trimer of an unsaturated fatty acid of about 10 to 20 preferably about 18 carbon atoms, sufficient trimer acid being present to give insolubles in the mixed product, and glyceride oil, especially a triglyceride oil, in amount sufficient to solubilize the trimeric unsaturated acid in the mineral oil. This invention thus relates to the solubilization of a low-cost mixture, such as about 5 percent, of dimer and trimer acids in highly refined mineral oil by using an amount of a glyceride oil such as triglyceride oil, sufficient to solubilize the mixture of dimer and trimer acids in the mineral oil. The glyceride oil or triglyceride oil is of at least 70 to 150 Iodine Number, preferably less than about 95 Iodine Number, e.g., peanut oil.

The amount of trimer often present in the dimer-trimer acid component is a minor proportion of these acids and usually at least about 5 or even at least about 10 weight percent of the total dimer and trimer acids. Sufficient glyceride oil or triglyceride is added to the product to solubilize essentially all of the trimer acid. The amount of glyceride oil or triglyceride oil employed is often at least about 10 or even at least about 20 weight percent of the composition and usually does not exceed about 30 weight percent. Various glyceride oils can be employed, such as soybean oil, peanut oil, their hydrogenated forms, etc. The unsaturated fatty acids useful in forming the dimer and trimer acids include, for instance, oleic acid, linoleic acid, ricinoleic acid, etc.

The mineral oil employed in my compositions 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 our 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 paraffinic carbon atoms.

The viscosity of the lubricating oil component of the compositions of this invention is such that the final 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 S.U.S. at 100° F. and often the viscosity does not exceed about 4,000 S.U.S. 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 nonforging steel, lower flashpoint 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 percent. The oil feedstocks often have a viscosity in the range of about 50 to 7,500 S.U.S. 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 1,500 to 5,000 p.s.i.g., weight hourly space velocities (WHSV) of about 0.1 to 1, and a hydrogen rate of about 1,000 to 5,000 s.c.f./B. Preferred operating conditions are temperatures of about 600° to 700° F., about 1,500 to 3,000 p.s.i.g. pressure, a WHSV of about 0.2 to 0.5, and hydrogen flow rate of about 1,000 to 3,000 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 1,000 to 5,000 p.s.i.g., WHSV of about 0.1 to 1, and a hydrogen feed rate of about 500 to 5,000 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 1,000 to 3,000 p.s.i.g., WHSV of about 0.25 to 0.5, and hydrogen flow rates of about 500 to 3,000 s.c.f./B.

The catalyst of the first hydrogenation operation can be of any of the sulfur-resistant, nonprecious 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 VIB 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 VIB constitute very satisfactory catalysts. Examples of such mixtures or compounds are nickel molybdate, tungstate, or chromate (or thiomolybdate, thiotungstate, 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 predominately calcined or activated alumina. Commonly employed catalysts have about 1 to 10 percent of an iron group metal and 5 to 25 percent of a Group VIB 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. No. 2,938,002.

As aforementioned, the catalyst of the second hydrogenation operation 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 preferred that it be so finely divided that it is not detectable by X-ray defraction means, i.e., that it exists as crystallites of less than about 50A. 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 predominately 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 mixture.

Following either of the hydrogenation operations 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 flashpoint 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 flashpoint 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 percent with 0 to 10 percent 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 may 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 (2,800° F.) like water on a hot pancake griddle. Eventually a dancing ball of lubricant struck and wet the cooler cooper 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 A

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 1,000 S.U.S. at 100° F. and a pour point of about −5° F. This oil is hydrogenated at 2,500 p.s.i.g. hydrogen partial pressure, 680° F., 0.25 weight hourly space velocity, and a hydrogen rate of 2,200 s.c.f. 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 2,500 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 2,500 s.c.f. of hydrogen per barrel of feed over a platinum on alumina catalyst containing 0.6 percent 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 S.U.S. at 100° F. A feedstock which can be used to product oil 3 at Table I can be derived from a mixed base crude oil and can be a dewaxed raffinate from the phenol treatment of the raw distillate, the dewaxed product having a viscosity of about 230 S.U.S. at 100° F.

In addition to the essential dimer and trimer unsaturated fatty acids and the glyceride or triglyceride oil, the mineral oil of lubricating viscosity may contain additives for improving pour point and viscosity index such as methacrylate ester polymers. These methacrylate ester polymers include a series of commercially available polymers known as the acryloids some of which are described in U.S. Pat. No. 2,710,842.

TABLE I

Product	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
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, Ramsbottom (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 example is illustrative of this invention:

EXAMPLE

The following formulation is typical of the lubricating compositions of the present invention. In this composition there was employed a mineral oil of lubricating viscosity prepared as in Example A having a carbon residue below about 0.1 percent (Ramsbottom) and an aromatic carbon contact less than about 1 percent and designated Mineral Oil A.

Table II

Composition	A
Mineral Oil A	74.0%
Soybean Oil	20.0%
Versadyme No. 228[1]	5.0%
Acryloid 150[2]	1.0%

*1 Versadyme No. 228 obtained from General Mills is a polymerized unsaturated vegetable fatty acid formed from primarily C_{18} unsaturated acids, and has the following characteristics:

Acid Value 191 (188–195)	
Saponification Value 199 (195–201)	
% monomer	3
% dimer	76
% trimer	21

*2 Acryloid 150 is a 40% concentrate in mineral oil of a methacrylate polymer in which the ester groups are derived from a mixture of alcohols in the C_8 to C_{14} range.

Product A was evaluated in a continuous steel (nonforging) casting operation. The mold size was 4¼×4¼ inches. In testing, Product A 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:

Table III

Test Results		
PRODUCT	A	
Smoke	Pass	
*Duration of Lubrication (sec.)	(Average 60	(Range) (55–71)
**Travel Test	Pass	

*time—the application product gave satisfactory lubrication at steel-mold interface; 15 seconds is borderline; 20 seconds is a solid pass.

**Measure of the ability of the lubricant to travel around the steel-mold interface.

A small volume of Product A, one-half pint, provided adequate lubricating for casting 12 tons of steel (e.g., two-thirds oz./ton or 0.015 gal./ton).

It is claimed:

1. A lubricating composition suitable for use in the continuous casting of metals to lubricate the mold metal interface which comprises lubricating amount of a mineral oil of lubricating viscosity having a carbon residue below about 0.1 percent (Ramsbottom) and an aromatic carbon content less than about 1 percent and from about 2 to 15 weight percent of total dimer and trimer of an unsaturated fatty acid of about 10 to 20 carbon atoms, sufficient trimer acid being present to give insolubles, and a glyceride oil in amount sufficient to solubilize the trimeric unsaturated acid in the mineral oil.

2. The composition of claim 1 in which the glyceride oil is present in amount up to at least about 30 weight percent of said lubricating composition.

3. The composition of claim 2 in which the dimer and trimer unsaturated fatty acid is an acid of 18 carbon atoms.

4. The composition of claim 1 wherein the total dimer and trimer of an unsaturated fatty acid is present in amount of about 3 to 10 weight percent of said lubricating composition.

5. The composition of claim 1 wherein the mineral oil of lubricating viscosity has a viscosity of at least about 100 S.U.S. at 100° F. and contains at least about 60 percent paraffinic carbon atoms.

6. The composition of claim 1 wherein the mineral oil of lubricating viscosity 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.

7. The composition of claim 3 wherein the mineral oil of lubricating viscosity 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.

8. The composition of claim 7 wherein the first stage catalyst has nickel or cobalt and molybdenum supported on alumina and the second stage catalyst is platinum-alumina.

9. A method of lubricating the metal-mold interface in the continuous casting of metals process which comprises providing a lubricating composition of claim 1 to said metal-mold interface.

10. A method of lubricating the metal-mold interface in the continuous casting of metals process which comprises providing a lubricating composition of claim 3 to said metal-mold interface.

11. A method of lubricating the metal-mold interface in the continuous casting of metals process which comprises providing a lubricating composition of claim 4 to said metal-mold interface.

12. A method of lubricating the metal-mold interface in the continuous casting of metals process which comprises providing a lubricating composition of claim 8 to said metal-mold interface.

13. The method of claim 9 in which the metal is steel.

14. The method of claim 10 in which the metal is steel.

15. The method of claim 11 in which the metal is steel.

16. The method of claim 12 in which the metal is steel.

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