

UNITED STATES PATENT OFFICE

2,355,995

WATER-SOLUBLE CUTTING COMPOSITION

John D. Morgan, South Orange, and Russell E. Lowe, East Orange, N. J., assignors to Cities Service Oil Company, New York, N. Y., a corporation of Pennsylvania

No Drawing. Application March 9, 1942,
Serial No. 433,938

11 Claims. (Cl. 252—48)

This invention relates to improvements in metal cutting compositions adapted to cool and lubricate metal cutting tools and the metal being cut. More particularly the invention relates to improved water soluble bases adapted to be used in the preparation of metal cutting compositions.

The present application is a continuation-in-part of the applicants' pending application Serial No. 389,760, filed April 22, 1941, for "Water soluble cutting compound and method of manufacture."

It has been discovered that certain of the intermediate reaction products obtained in accordance with the disclosure of this prior application may be used in conjunction with the water soluble material thereof in the making of improved cutting compositions.

According to the present invention, the improved cutting compositions or bases include: (1) as a principal constituent a water soluble material obtained by chlorinating, phosphorizing and sulfonating a heavy petroleum oil (hereinafter identified as product C); (2) a substantial proportion of a chlorinated, phosphorized and sulfonated oil (hereinafter identified as product B); (3) a relatively small proportion of a glycol ester such for example as diglycol laurate; (4) a relatively small proportion of a high molecular weight fatty acid such for example as oleic acid, and (5) a relatively small proportion (0.2 to 0.6%) of an oxidation inhibitor such as triethanolamine or other water soluble organic amine. The cutting composition or base may also include from a relatively small proportion up to a substantial proportion of a chlorinated and phosphorized oil (hereinafter identified as product A).

Since some of the products used in the compositions of the present invention are preferably made in accordance with the disclosure of the above-mentioned pending application, it will be noted that according to the procedure therein disclosed, a crude petroleum oil is converted to produce an intermediate reaction product by reacting the crude oil at moderate temperature with an active inorganic halide and chlorine in the presence of a catalyst. The intermediate reaction product is thereupon subjected to a sulfonation operation to produce a tarry mass which is diluted with water, neutralized to Congo red indicator and concentrated to provide the base for the metal cutting compound.

The pending application describes a specific example in which a batch of Duvall crude oil having an A. P. I. gravity of about 21 and comprising 275 cc., was heated to a temperature of from 300° to 350° F. and introduced into a vertical retort substantially filled with loose graphite chips. The retort was maintained in this temperature range, and a small stream of chlorine gas was

introduced into the bottom of the retort and bubbled through the oil therein at a rate of about one gram per minute. After the flow of chlorine had been started through the retort, the upper end thereof being vented, 5 cc. of PCl_3 was slowly introduced into the bottom of the retort and flushed in with an additional 50 cc. of the Duvall crude oil. These steps required eight or ten minutes, after which the introduction of the chlorine was continued for a period of thirty minutes, while the temperature in the retort was held within the range of 300° to 350° F.

The intermediate reaction product formed by the above procedure was withdrawn from the retort through a drawoff valve at the bottom and comprised approximately 323 cc. of liquid having a specific gravity of 0.93 (300 gms.). The retort was found to be clean and free of any sludge. The 300 grams of intermediate product (product A referred to above) was cooled to room temperature and then treated with 45 grams of chlorosulfonic acid, added slowly to avoid overheating and foaming, and the resulting mixture was permitted to react with mild stirring for a period of about two hours. The resulting material comprised an upper layer of black tarry viscous material, and a lower liquid oil layer which was separated out and recovered. This oil is the product B referred to above and is used directly in the improved compositions. The tar-like material comprising 138 gms. was dissolved in 290 cc. of water, by warming, and was then neutralized to Congo red with a 25% solution of sodium hydroxide, 17 grams of NaOH being required.

The neutralized material comprising approximately 493 gms. was concentrated by evaporation to about 146 gms. The resulting concentrate separated into two layers, the upper of which was a brown viscous mass, while the lower layer comprised a highly fluorescent aqueous solution. The upper layer of 123 gms. and comprising the desired product, was dissolved in water to give a specific gravity of from 1.055 to 1.065, then settled (centrifuging may be used) to remove any water-insoluble residue. In this instance 350 gms. of water were required to give the solution a specific gravity of 1.060. This material is a concentrate which may have a gravity of from 1.040 to 1.065, and is not intended to be used directly, but should be diluted to at least approximately 20 to 1 with water.

This concentrate is the water soluble product C referred to above. This material is a water solution comprising about $\frac{3}{4}$ water and upon further dilution gives a clear or transparent solution even with rather hard water. The product has a water hardness tolerance in excess of 225 parts per million, and in dilutions of 20 to 1, it has the ability to inhibit staining or corrosion, including rusting of iron and steel. The concen-

trate has a pH of approximately 5.2 which may be brought up to a value in excess of 7 by the addition of dilute sodium hydroxide until the concentrate is alkaline to red litmus. The effectiveness of this water soluble material, product C when used alone in a cutting composition even up to dilutions of 1 to 50 with water was found to be superior to a known commercial cutting composition.

The pending application describes the characteristics of Duvall crude oil and points out that while the use of naphthenic petroleum oils were preferred (of the type of Duvall), other heavy petroleum oils could be used in the process described above. Placedo crude oil has been used. It was also pointed out that the conversion reaction may be carried out in the presence of other catalysts which are equivalent to graphite, as for example, activated carbon, activated charcoal, silica gel and other adsorbent catalysts such as activated clays and fuller's earth; that such reaction carried out in the retort may also be promoted by other active inorganic halides which are equivalent to the preferred PCl_3 , such for example as AlCl_3 , BCl_3 , FeCl_3 , AlBr_3 , SbCl_3 , SnCl_3 , and ZnCl_2 ; that instead of using chlorine, other equivalent chlorinating agents adapted to chlorinate some of the constituents in the oil could be employed; and that other sulfonating agents such as SO_3 , fuming sulfuric acid, and other equivalent agents may be used for the sulfonation operation.

The pending application also points out that the chemical constitution of the water soluble material, product C, was not known, but that its exceptional quality and effectiveness was believed to be due at least in part to the simultaneous treatment of the high gravity oil with the chlorinating agent and the active inorganic halide; and that the preferred product comprised carbon compounds containing chemically combined phosphorus, chlorine and sulfonate groups, other electropositive atoms of active inorganic halides being useful in place of phosphorus.

From the foregoing description of the procedure for making certain of the improved ingredients for use in the cutting compositions of the present invention, it should be apparent that considerable variation in the compositions may be made. However, the following examples will serve to illustrate cutting composition bases in accordance with the present invention, the percentages being by volume.

Example 1

A preferred base composition adapted to be used at dilutions of from 1 to 10 up to 1 to 40, with water, is as follows:

	Per cent
(1) Mixture of water-soluble carbon compounds containing combined phosphorus, chlorine and sulfonate groups, in a water solution of 1.050 sp. gr. (product C) -----	83.75
(2) Oil containing combined phosphorus, chlorine and sulfonate groups (product B) -----	12
(3) Diglycol laurate -----	3
(4) Oleic acid -----	1
(5) Triethanolamine -----	0.25

In preparing the cutting composition base from these constituents, the concentrate, product C, is preferably diluted three to one with water, a mixture is made of the oil product B, the diglycol laurate and the oleic acid and this mixture is 75

then incorporated into the water solution. Finally the triethanolamine is added to complete the base composition. While the above dilution of three to one applies in the case of products from Duvall crude, a corresponding dilution of four to one was used in the case of Placedo crude with the same specific gravity of 1.050 for the concentrate.

A cutting composition for special and extreme conditions is made with one part of the above base mixture and ten parts of water. A standard product will have a dilution ratio of 1 to 20.

Example 2

A water soluble base for preparing cutting compositions by addition of water has the following constituents:

	Per cent
(1) Mixture of water-soluble carbon compounds containing combined phosphorus, chlorine and sulfonate groups in a water solution of 1.050 sp. gr. (product C) -----	81.75
(2) Oil containing combined phosphorus, chlorine and sulfonate groups (product B) -----	10
(3) Diglycol laurate -----	3.0
(4) Oleic acid -----	1
(5) Triethanolamine -----	0.25
(6) Heavy hydrocarbon oil containing chemically combined chlorine and phosphorus groups (product A) -----	4

The oils A and B, the diglycol laurate and the oleic acid are preferably mixed and then added to the diluted product C, as in Example 1, the triethanolamine being added last.

The cutting compositions may have the same dilutions as in Example 1.

Example 3

A water soluble base for preparing cutting compositions by addition of water has the following constituents:

	Per cent
(1) Mixture of water-soluble carbon compounds containing combined phosphorus, chlorine and sulfonate groups in a water solution of 1.050 sp. gr. (product C) -----	81
(2) Oil containing combined phosphorus, chlorine and sulfonate groups (product B) -----	8
(3) Diglycol laurate -----	3
(4) Oleic acid -----	1
(5) Triethanolamine -----	0.25
(6) Heavy hydrocarbon oil containing chemically combined chlorine and phosphorus groups (product A) -----	6.75

The base composition is preferably made up in accordance with the procedure of Examples 1 and 2. The dilutions of the base for the preparation of the cutting compositions may be the same as in Example 1.

The oil products A and B, used as constituents in the bases of the foregoing examples are not normally soluble in water but are brought into solution or into a very intimate colloidal dispersion in water by the water soluble product C, the diglycol laurate, the triethanolamine, and the oleic acid. The product C is a water solution of which only a small proportion is carbon compounds, produced by the above described process. Cutting compositions which include both of the oils A and B are practically clear solutions but in

some cases may have a slight opalescent appearance. The oil product A is preferably only used in making up the bases to replace a portion of the oil product B so that the proportion of the water soluble product C or solution is not reduced much below about 80% by volume. The proportion of A is preferably less than that of B.

The diglycol laurate, in addition to aiding in the dispersion or solution of the oil products A and B, also acts as a corrosion inhibitor and as a plasticizer. The plasticizing action of the laurate is made use of primarily after the cutting operation is completed and the work is left coated with the coating composition. The laurate prevents the formation of a dry brittle coating. The oleic acid functions primarily as a dispersing agent for the oil products A and B and as a plasticizing aid.

Various other base compositions may be made from the constituents listed above or their equivalents. The content of product C or its equivalent may vary from about 80% to 85%, that of product B from 8% to 12%, and that of product A when used, from 1 to 7%. Instead of using diglycol laurate, other diglycol esters of high molecular weight fatty acids may be used, and these or the laurate may comprise from about 2% to 4% of the base mixture, 3% however being preferred. Other fatty acids than oleic acid may be used, such as other well-known high molecular weight fatty acids, as stearic and linoleic. The percentage of this constituent may vary from 0.5% to 1.5%. The final diluted product should preferably have a pH value of from 7.2 to about 7.6.

Having described the invention in its preferred form, what is claimed as new is:

1. A metal cutting base composition comprising approximately 83.75% of a water-soluble product including chlorinated, phosphorized and sulfonated mineral oil, approximately 12% of a normally water-insoluble oil product including a chlorinated, phosphorized and sulfonated mineral oil, 3% of diglycol laurate, 1% of oleic acid, and approximately 0.25% of a water soluble organic amine.

2. A metal cutting base composition comprising approximately 82% of a water-soluble product including chlorinated, phosphorized and sulfonated mineral oil compounds, approximately 10% of a normally water-insoluble chlorinated, phosphorized and sulfonated mineral oil, approximately 4% of a normally water-insoluble chlorinated, phosphorized mineral oil, approximately 2.5% of a di-glycol ester, approximately 1% of a high molecular weight fatty acid, and approximately 0.5% of a water-soluble organic amine.

3. A metal cutting base composition compris-

ing from about 80% to about 85% of a water-soluble product including chlorinated, phosphorized and sulfonated constituents of mineral oil, from about 8% to about 12% of a normally water-insoluble chlorinated, phosphorized and sulfonated mineral oil, from about 2% to 4% of di-glycol laurate, from 0.5% to 1.5% of oleic acid, and from 0.2% to 0.6% of a water-soluble organic amine.

4. A metal cutting base composition comprising from about 80% to about 85% of a water-soluble product including chlorinated, phosphorized and sulfonated constituents of mineral oil, from about 8% to about 12% of a normally water-insoluble chlorinated, phosphorized and sulfonated mineral oil, from 1% to about 7% of a normally water-insoluble chlorinated and phosphorized mineral oil, from about 2% to 4% of a di-glycol ester, and from 0.5% to 1.5% of a high molecular weight fatty acid.

5. A metal cutting base composition as defined by claim 3 in which said water-soluble product is a solution, at least about three-fourths of which is water.

6. A metal cutting base composition as defined by claim 3 in which said mineral oil is a naphthenic base petroleum.

7. A metal cutting base composition as defined by claim 4 in which said water-soluble product is a solution of which about three-fourths is water.

8. A metal cutting base composition as defined by claim 4 in which said mineral oil is a naphthenic base petroleum.

9. A metal cutting base composition as defined by claim 3 in which said water-soluble product is substantially diluted with water, a mixture made of said water-insoluble oil, said laurate and said oleic acid, and the resulting mixture incorporated into said diluted product.

10. A metal cutting base composition as defined by claim 4 in which said composition is made up by diluting said water-soluble product substantially with water, mixing said water-insoluble oils, di-glycol ester and said fatty acid together, and thereafter incorporating the resulting mixture into the diluted water-soluble product.

11. A metal cutting base composition adapted for use in a dilute water mixture, comprised principally of chlorinated, phosphorized and sulfonated mineral oil constituents including water-soluble and water-insoluble compounds, and from about 2% to about 4% of a diglycol ester of a high molecular weight fatty acid as a plasticizer and metal corrosion inhibitor for the coating left on the metal after it has been cut.

JOHN D. MORGAN.
RUSSELL E. LOWE.