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PRODUCTION OF FOAM INHIBITOR

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The present invention relates to a novel method of preparing compositions which are characterized by the property of destroying and inhibiting foam formation. The compositions prepared by the method of the present invention are gels comprising as essential constituents a liquid organic medium, a microcrystalline wax and a polymer of ethylene.

Metal working oils, such as soluble emulsifiable cutting oils, are frequently employed under conditions which include extreme agitation and high pressure application. The conditions cooperate to effect lubrication and cooling but disadvantageously produce foam. Foam can interfere with visual control of the operation being effected, can insulate the piece being worked from the cooling action which the lubricant otherwise exerts and can escape the immediate work area and result in unsatisfactory operating conditions. Accordingly, it is frequently undesirable that foam, especially stable foam, be produced during metal working operations.

As disclosed in application Serial No. 561,666 to Lawrence A. Roehler, filed January 26, 1956, now U.S. Patent No. 2,972,578, the addition of the gels with which the present invention is concerned to a soluble oil results in a composition characterized by the ability to resist formation of and to destroy foam occurring during use. As described in the mentioned application, the gels of the present invention have been prepared by adding the polymer and wax to the material which comprises the liquid organic medium together, or one at a time, treating in a manner that effects solution and then rapidly cooling or chilling the mixture to obtain the gel. Rapid chilling has been used in the production of gels of the most satisfactory characteristics. This necessity of rapid chilling has naturally presented certain difficulties with respect to adequate cooling. For instance, it has been found, that in attempting to produce a satisfactory gel in warm climates such as during summer months of peak ambient temperature, employment of ordinary cooling media such as ambient temperature water or air fails to effect the required rapid cooling so that the most advantageous gel formation is not obtained. Consequently, a less effective foam suppressor is produced unless inconvenient and more expensive cooling methods are relied upon such as refrigerating means, ice cooled water, ice packs, etc., to overcome this difficulty. The problem has become severe and the previously employed method highly impractical when it is desired to produce large quantities of the gel throughout the year without provision of special cooling means.

We have now discovered a method of producing the gels of the present invention without resorting to rapid cooling; and, moreover, close control of temperature and time of ingredient addition is of little, if any, significance. In accordance with our method the ethylene polymer and wax are added to the organic liquid which comprises the organic medium, together or one at a time, and the mixture is at or is heated to a temperature sufficient to effect solution of the polymer and wax. The mixture is then cooled to a temperature below the cloud point of the mixture, preferably at least about 5° F. below the cloud point, and again reheated to a temperature within the range of immediately above the cloud point of the mixture, e.g. at least about 1° F. above, to about 20° F. above the cloud point, preferably up to about 10° F. above the cloud point and not above about 170° F., to effect resolution. The mixture is then permitted to cool to below about 120° F., usually to room temperature. If desired, the cooling steps employed can be hastened by use of any suitable cooling means but in accordance with the present invention this is unnecessary. As a result of the present method a satisfactory and effective gel is obtained by merely allowing the mixture to cool by itself without the application of external cooling means. Thus cooling to solidify the wax and polyethylene after their initial solution can be relatively slow as can the cooling after reheating to just above the cloud point. By following the reheating procedure a mixture of oil, polyethylene and wax of insufficient foam inhibiting properties is transformed to a product significantly improved in this respect.

A very advantageous method of producing these gels in accordance with our method, which has been developed for commercial scale production, comprises putting about 25 to 75% of the base organic medium into a kettle, adding all of the ethylene polymer to be employed and heating the mixture to a temperature sufficient to melt the polymer, for example, about 200 to 240° F. After the polymer is melted, the wax is added and allowed to melt. About 25 to 40% of organic medium is then added and the mixture cooled, for instance, by circulating water, until the cloud point is reached. The remaining organic liquid is added and the cooling continued preferably until the temperature of the mixture is more than about 10° F. below the cloud point. At this point the mixture is reheated until the temperature is just above the cloud point and preferably not materially above about 170° F. The cloud point is generally at least 140° F. The mixture is then permitted to cool to below about 120° F., usually to ambient temperature.

The compositions of the invention can be employed in lubricants in metal working operations, especially soluble cutting oils. Soluble cutting oils are well known commercial products generally comprising a refined lubricating oil base, a soap or other emulsifying agent and a common solvent and/or coupling agent, the materials being present in amounts such that a stable emulsion can be formed by the composition and about 1 to 50 parts of water. Typical soluble oils comprise a lubricating oil base, about 10 to 25 weight percent of an emulsifier such as a sulfonate, naphthenate or oleate, about 3 to 7 weight percent of a secondary emulsifier such as sodium rosinate or analogous metal salt, and about 0.5 to 1.0 weight percent of a coupling agent such as ethyl or butyl Cellosolve (glycol ethyl ether or glycol butyl ether) or diethylene glycol. Additives such as bactericides and extreme pressure agents and the like also are frequently included to advantage.

For best service it has been found that compounding of the soluble oil and our gel should be accomplished under certain conditions. For example, it has been found that the prepared additive should not be incorporated in the soluble oil when the temperature of the soluble oil is greater than about 150° F. Thus, we disperse the additive in the soluble oil at a temperature of about 100° F. while mildly agitating, and temperatures of about 70° F. to 125° F. have been found to be particularly satisfactory. The most advantageous temperature to be employed is determined primarily by the quantity of additive used. For example, with about 3% additive a temperature of about 100° F. is most desirable while with 5%, temperatures of about 120° to 125° F. appear to be optimum. The invention can also be practiced by dispersing the additive components directly into the soluble oil at temperatures of gel formation as mentioned above rather than preforming the additive composition and then adding it as such. In this instance also the use of high tempera-

tures, that is above about 150° F. after the additive has formed should be avoided. The anti-foam additive is employed in soluble oils in an amount effective to inhibit formation of and destroy foam occurring in use. Generally about 0.05 to 20 weight percent of the additive, and particularly 3 to 7 weight percent, is employed, based on the resulting soluble oil-additive composition and depending upon the soluble oil used and the use contemplated.

The polymeric materials employed in the present invention are known articles of commerce. They are polymers of ethylene having molecular weights of about 1000 to 12,000, preferably about 1500 to 2500. The polymers generally are used in amounts of about 1 to 10 weight percent of the gel composition, and preferably about 1 to 4 weight percent. In addition to the usual ethylene polymers, terminal hydroxyl-containing polymers of ethylene conforming to the preceding physical properties also can be used. In fact, the preferred polymers are terminal hydroxyl-containing polymers of ethylene having a molecular weight of about 2000 to 2200. In general, terminal hydroxyl-containing polymers are prepared by polymerizing ethylene at the usual conditions of temperature and pressure, that is at pressures from about 800 to 3000 atmospheres and temperatures from about 390 to 750° F., with or without a free radical forming catalyst such as hydrogen peroxide and in the presence of a hydroxyl-containing chain stopper such as isopropanol. Commercially available examples of satisfactory hydroxyl-containing polymers are Alcowax No. 6 and No. 7, available from Allied Chemical and Dye Company. Conditions for the preparation of these materials are well-known as is evidenced by U.S. Patents No. 2,504,400 and No. 2,683,141. By terminal hydroxyl-containing we intend to indicate that a hydroxyl radical is on one of the end 5 or 10 carbon atoms rather than being centrally located in the molecule; it is believed that the hydroxyl radical generally occurs on one of the end three carbon atoms.

The micro-crystalline wax component which can be used in the present invention is an article of commerce produced from petroleum oils. Microcrystalline waxes are obtained from Pennsylvania or Mid-Continent crude oils and are generally characterized by a large percentage of non-normal paraffins and advantageously melt in the range from about 120 to 200° F. (PMP). Typical properties include a petrolatum melting point (PMP) from about 165 to 175° F., a viscosity at 210° F. of about 65 to 80 Saybolt Universal Seconds and a penetration at 77° F. of about 11 to 14. The wax is usually about 2 to 10 weight percent of the gel composition, preferably about 3 to 8 percent.

The major portion and preferably the substantial balance of the novel gel compositions of this invention comprises a liquid organic medium, for example a suitable oil. Suitable oils are those of lubricating oil viscosity and preferably those having a viscosity at 100° F. ranging from about 50 to 150 SUS. Oils which are too light may result in bleeding in the resulting gels and those which are too heavy frequently render the gels difficult to disperse in soluble oils. The oils preferably are mineral base and can be obtained from any known crude. Particularly satisfactory oils include naphthenic base lubricating oil fractions having a viscosity of about 100 SUS at 100° F. Other suitable oils include kerosene, gas oils and other liquid mineral oil fractions. These petroleum oils can be replaced with other liquid organic mediums such as fatty oils, alcohols, polyamine, polyalcoholpolyethylene oxide condensation products, diester synthetic lubricants and so on, so long as a satisfactory gel results upon its use.

Thus typical compositions include a gel composed, for example, of a liquid organic medium, about 2 to 10 weight percent of the wax and about 1 to 10 weight percent of ethylene polymer. A typical specific composition is a gel containing a naphthenic base lubricating oil fraction having a viscosity of 100 SUS at 100° F., 5 weight percent of a paraffin base microcrystalline wax having a PMP melting point of about 165° F. and 2 weight percent of a polymer of ethylene having a molecular weight of 1800. In the soluble oil compositions, a typical specific composition is 5 weight percent of the above specific gel dispersed in a soluble oil consisting of a Mid-Continent base lubricating oil having a viscosity at 100° F. of 125 SUS, 15 weight percent of sodium mahogany sulfonate, 5 weight percent of sodium rosinate and 2 weight percent of diethylene glycol. All percentages are by weight percent based on the resulting compositions, unless otherwise specified. While a gel is the specified and preferred physical state of use, the composition can be used as a liquid provided it has first been a gel.

In addition to the components of the gel compositions described, and of the soluble oils where employed, the compositions can also contain other additives commonly employed in the art in the usual amounts so long as the foam depressing and foam breaking properties are not unduly deleteriously affected. Such additives include antioxidants, wetting agents, extreme pressure agents, anti-staining agents and so on.

The invention will be described further in connection with the following specific example. It should be understood that the details disclosed are not intended as limiting the invention.

Example

60 grams of a terminal hydroxyl-containing polymer of ethylene having a molecular weight of 2100 and 960 grams of a refined naphthenic base lubricating oil having a viscosity of about 100 SUS at 100° F. were charged to a kettle and heat was applied with stirring. The ethylene polymer was in solution in the oil after twenty-five minutes. The temperature of the batch was held at 215° F. Heat was stopped and 15 percent by weight (based on the oil and polyethylene previously combined) of paraffin base microcrystalline wax was added and allowed to melt. The temperature dropped to 196° F. after 15 minutes with stirring. 970 grams more of the oil was added and essentially ambient temperature water cut into the water jacket of the kettle. Stirring was continued until the cloud point (160°) was reached. The remainder of the oil (970 grams) was added with the cooling water still in use and stirring was continued. The temperature dropped to 140° F. The cooling water was stopped and the reheat cycle started and continued until the temperature was above the cloud point (160° F.). The heating was stopped at 170° F., the cooling water run into the jacket to remove the steam and then cut out. Stirring was continued until the cloud point was reached and the batch was allowed to cool to room temperature (78° F.).

Three weight percent of the product thus formed was added to a commercial soluble oil maintained at about 100° F. The properties of the commercial soluble oil were as follows:

Gravity, ° API	21.8
Flash, ° F.	320
Fire, ° F.	380
SUS at 100° F.	317.9
SUS at 212° F.	50.63
Pour, ° F.	5

The soluble oil-gel composition was tested in the Pontiac C–60 Foam Test. The composition passed the test giving 1100 millimeters of foam with a break time of 7 seconds using a diffusion stone that delivered 10,000 cc. of air per minute at a pressure of 34 inches.

We claim:

1. A method for producing a gel consisting essentially of a major amount of a mineral oil of lubricating viscosity, about 1 to 10 weight percent of an ethylene polymer having a molecular weight of about 1000 to 12,000, and about 2 to 10 weight percent of a petroleum microcrystalline wax, said method comprising heating the mix-

ture of said oil of lubricating viscosity, ethylene polymer, and micro-crystalline wax at a temperature sufficient to provide solution, cooling the mixture to a temperature below the cloud point of the mixture, reheating the cooled mixture to a temperature within the range of immediately above the cloud point of the mixture to about 20° F. above the cloud point, and cooling the mixture to a temperature below about 120° F.

2. The method of claim 1 wherein the ethylene polymer has a molecular weight of about 1500 to 500.

3. The method of claim 2 wherein the ethylene polymer is a terminal hydroxyl-containing polymer of ethylene.

4 The method of claim 3 wherein the maximum reheating temperature is about 170° F.

5. A method for producing a gel consisting essentially of a major amount of a mineral oil of lubricating viscosity, about 1 to 4 weight percent of a polymer of ethylene having a molecular weight of about 1000 to 12,000 and about 3 to 8 weight percent of a petroleum microcrystalline wax, said method comprising heating about 25 to 75% of said mineral oil of lubricating viscosity, ethylene polymer and microcrystalline wax at a temperature

of about 200 to 240° F. to provide solution, adding about 20 to 40% of said mineral oil, cooling the mixture to the cloud point, adding the remainder of said mineral oil, cooling the mixture to a temperature at least about 10° F. below the cloud point of the mixture, reheating the cooled mixture to a temperature within the range of 10 to 20° F. above the cloud point, and cooling the mixture to a temperature below about 120° F.

6. The method of claim 5 wherein the ethylene polymer is a terminal hydroxyl-containing polymer of ethylene having a molecular weight of about 2000 to 2200, and the maximum reheating temperature is about 170° F.

7. The method of claim 6 wherein the solution of mineral oil, hydroxyl-containing ethylene polymer and microcrystalline wax is obtained by first heating the polyethylene and oil at temperatures providing solution and then adding the microcrystalline wax to the resulting solution at temperatures providing solution of the wax.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 10, for "500" read -- 2500 --.

Signed and sealed this 8th day of October 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWIN L. REYNOLDS
Acting Commissioner of Patents