May 4, 1937. F. W. SULLIVAN, JR., ET AL 2,079,051

LUBRICATING OIL

Filed March 15, 1933 3 Sheets-Sheet 1

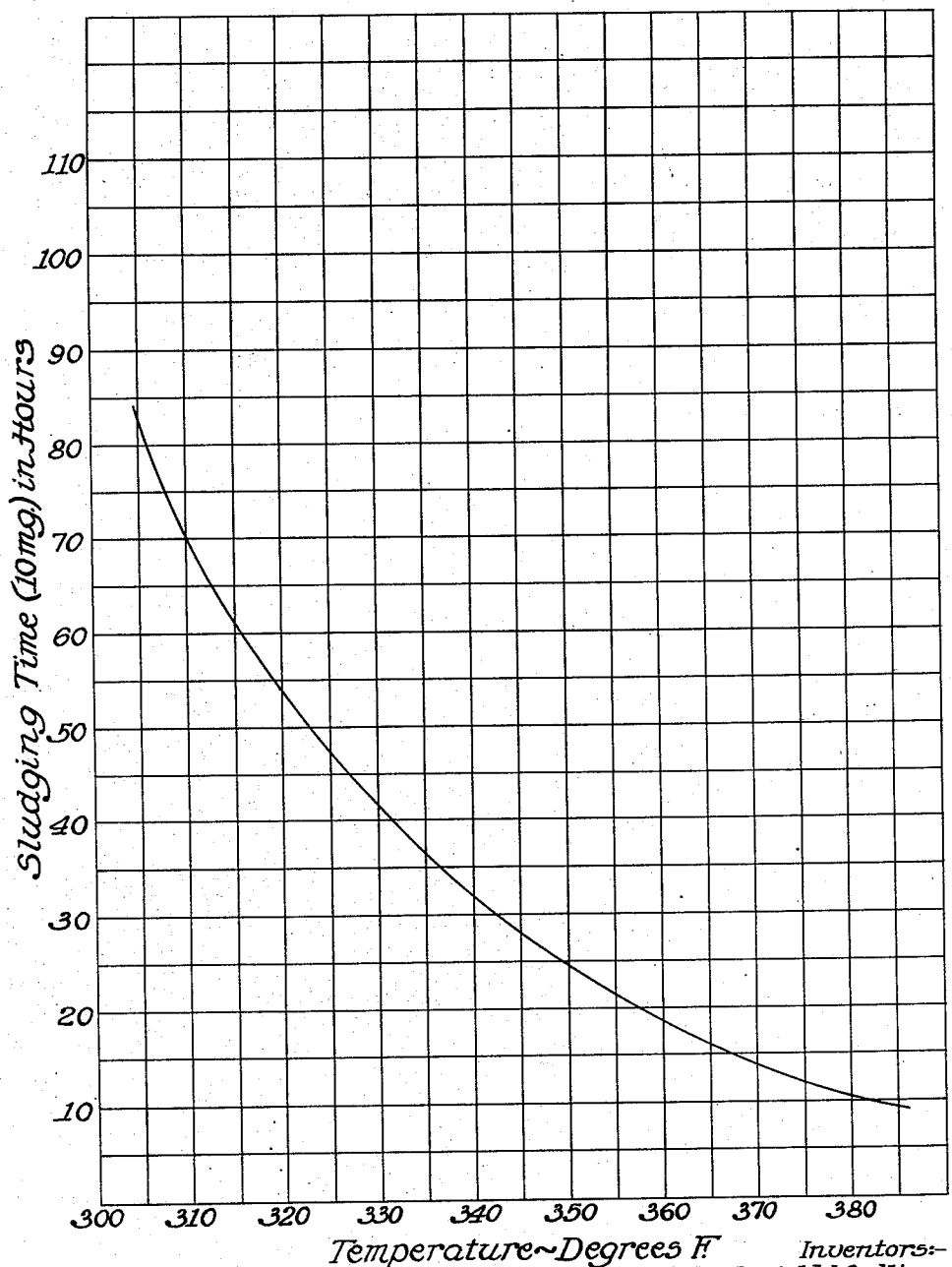


Fig. 1

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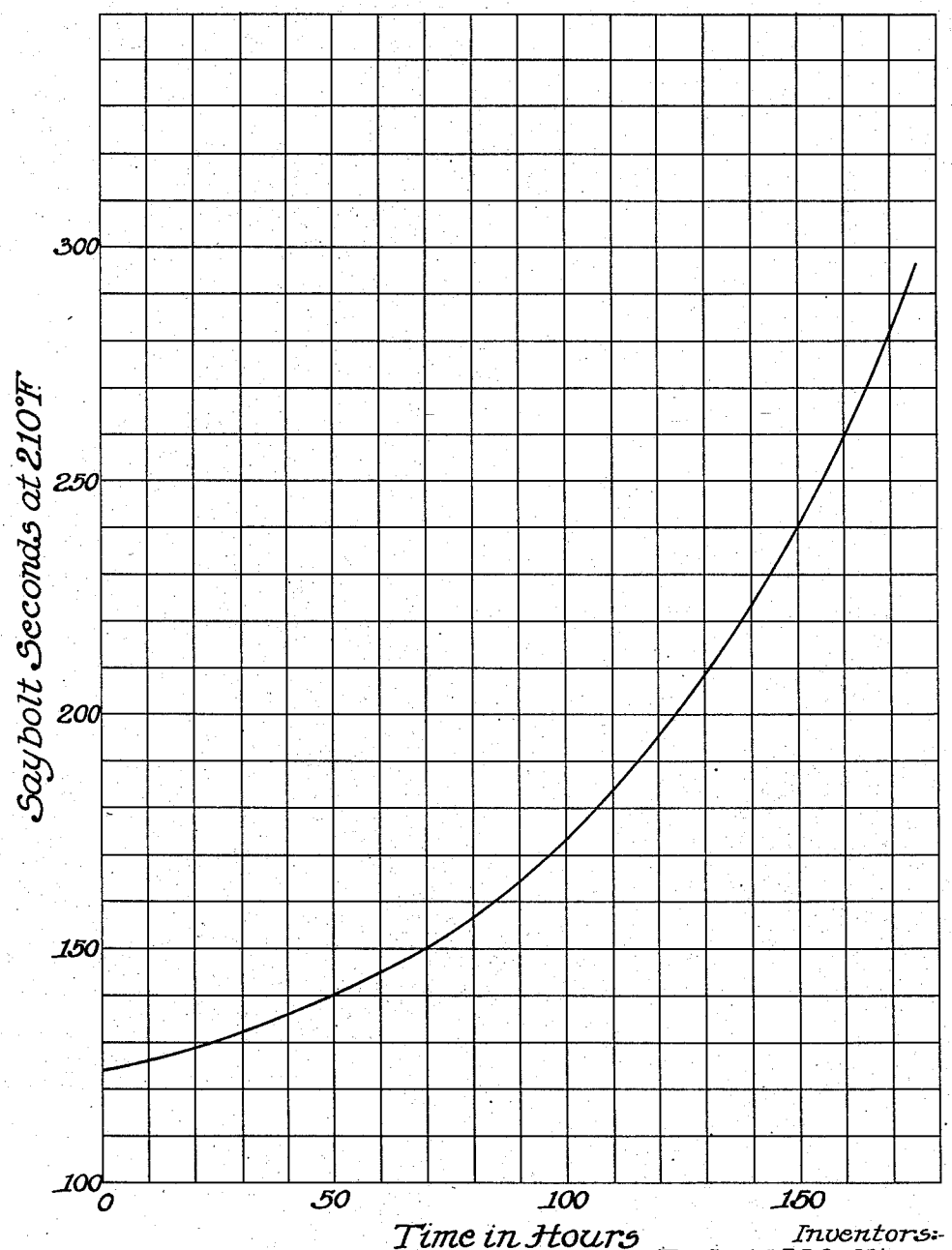


Fig. 2

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Filed March 15, 1933 3 Sheets-Sheet 3

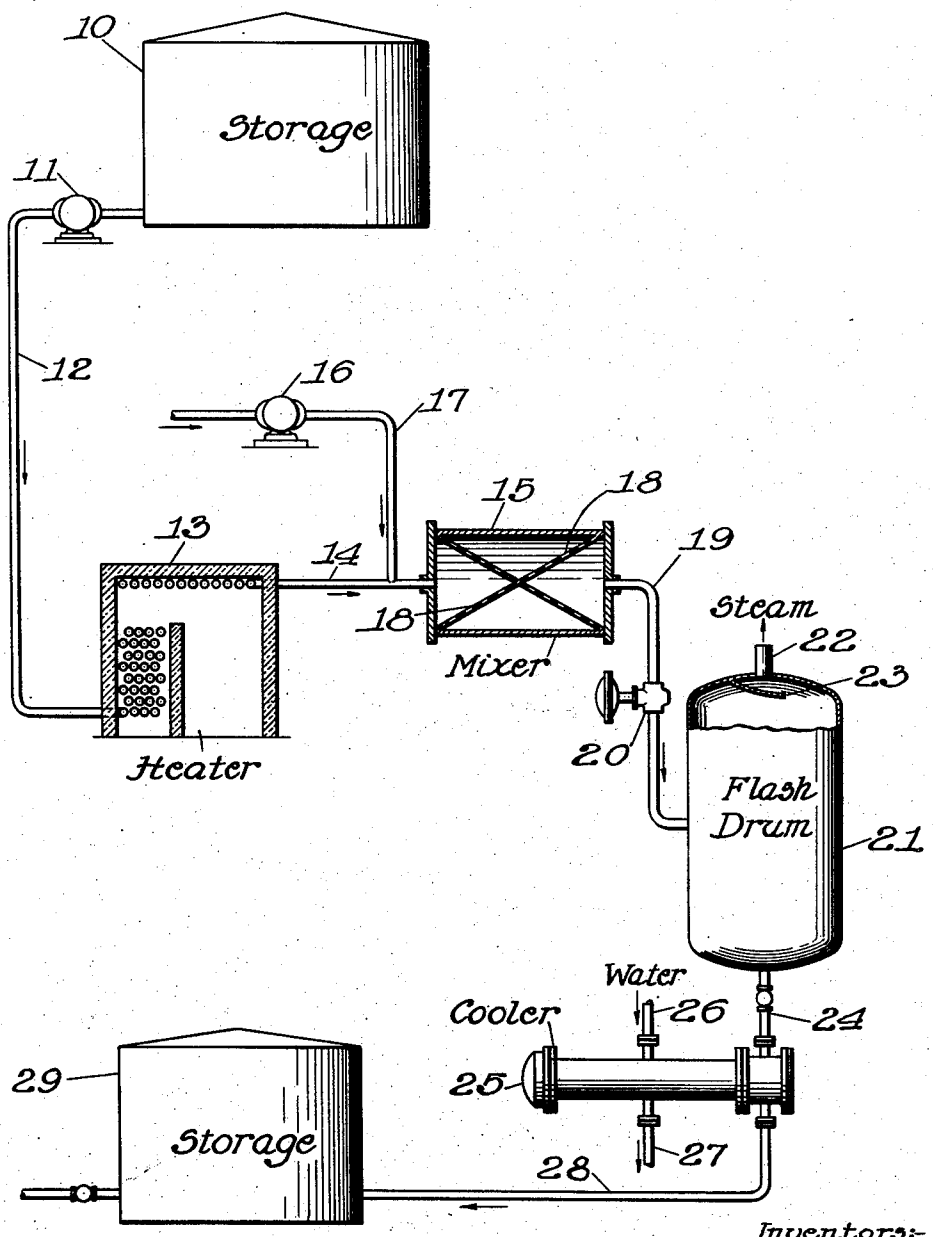


FIG. 3

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Patented May 4, 1937 2,079,051

UNITED STATES PATENT OFFICE

2,079,051

LUBRICATING OIL

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Application March 15, 1933, Serial No. 660,864

5 Claims. (Cl. 87—9)

This invention relates to the stabilization of mineral oils and it pertains more particularly to a process and composition for preventing sludge and color formation in lubricating oils when used under conditions conducive to oxidation.

Mineral oils, and particularly refined lubricating oils, when used in internal combustion engines or under conditions where the oils come in contact with hot surfaces, or oxygen, deteriorate and form sludge, color and varnish-like products that deposit on the surfaces being lubricated, and the viscosity of the oil increases with use. This deterioration of mineral oils is particularly noticeable with oils used to lubricate internal combustion engines. The sludge formed collects on the piston rings and causes them to stick. Also, sludge collects in the oil pumps and oil lines and greatly retards the flow of oil and in some cases plugs up the lines and small passages.

The object of our invention is to provide a method for stabilizing mineral oils and particularly lubricating oils against deterioration.

Another object is to provide a method of inhibiting sludge formation in mineral oils by adding to the oil an inhibiting agent.

Another object is to prevent the increase in viscosity of the oil upon continued use. Another object is to provide a method for preventing color deterioration of the oils.

A further object is to provide a method for preventing the formation of varnish-like products in lubricating oils and the staining of the parts to be lubricated.

A brief description of the figures of the drawings is as follows:

Fig. 1 is a curve which illustrates the tendency of a heavy Mid-Continent lubricating oil to form sludge with increase in temperature.

Fig. 2 is a curve which illustrates the tendency of mineral oils to increase in viscosity upon use.

Fig. 3 is a plan view, partly in section, of an apparatus, for dispersing alkaline materials in oil.

In internal combustion engines, it is very important that the lubricating oils be stable against sludge formation. We have found that motor oils have a marked tendency to form sludge and deteriorate at the high operating temperatures generally encountered in internal combustion engines such as are used in automobiles and aeroplanes. At these high temperatures it is common for lubricating oils to decompose and form sludge and coke on the pistons and in the ring grooves of the pistons. This results in sticking of the rings which, in turn, allows more oil to gain access to the cylinders, thereby aggravating the condition and causing excessive oil consumption and loss of compression. The curve in Figure 1 illustrates the tendency of a heavy Mid-Continent lubricating oil to form sludge with increase in temperature. It will be observed that at 320° F. it requires about 54 hours for 10 grams of oil to form 10 milligrams of sludge, whereas at 360° F. it requires only 18 hours to form 10 milligrams of sludge. It is very important to note that a relatively small increase in temperature will greatly increase the amount of sludge formed. The sludge stability of the oil with reference to temperature, shown in Figure 1, was determined by heating a quantity of oil to the temperature in question and bubbling air through the sample at the rate of 10 liters per hour. At intervals, 10 gram samples were withdrawn and tested to determine the amount of sludge formed in each 10 grams of oil. When the amount of sludge has increased to 10 milligrams the number of hours of oxidation is noted and the sludge stability of the oil is then expressed in hours required to form 10 milligrams of sludge per 10 grams of oil. The amount of sludge is determined by diluting the 10 gram sample of oxidized oil with hexane, filtering off the hexane insoluble residue, and then washing the filter repeatedly with hexane, the residue being sludge. This method is described in the American Society of Testing Materials Proceedings, volume 24, page 967.

Another undesirable characteristic of lubricating oils is their increase in viscosity upon use. The curve shown in Figure 2 illustrates this property of mineral oils. It will be observed that the Saybolt viscosity increases greatly upon use. The results expressed by the curve in Figure 2 were obtained by maintaining a Pennsylvania oil at 340° F. and bubbling preheated air through the oil at the rate of 100 to 150 liters per hour. It is apparent that when mineral oils are used at elevated temperatures in internal combustion engines and the like, the viscosity increases upon continued use and the oil becomes so viscous that a heavy load is put upon the engine, especially when starting. This is particularly noticeable in cold weather.

Another common and undesirable property of mineral oils, and particularly those lubricating oils used in contact with hot surfaces, such as internal combustion engines, is the development of color. We have found that by dispersing a small

amount of an alkaline material therein, hereinafter described, the color of the oil can be stabilized for long periods of time without substantial deterioration.

We have found that hydrocarbon oils, and particularly lubricating oils, can be stabilized against deterioration as illustrated by sludge formation, increase in viscosity upon use, staining of the surfaces to be lubricated and color formation, by dispersing in the oil a small quantity of an alkaline material such as the alkali metal salts of volatile organic acids and particularly those salts that dissociate on heating. We have found that the alkali metal salts, including magnesium salts, of volatile organic acids such as acetic acid, propionic acid, benzoic acid and formic acid, are particularly suitable for this purpose. Other alkali metal salts of acids may be used, for example, the salts of carbonic acid, sulfurous acid and hydrogen sulfide. Also the alkali metal hydroxides may be used, for example, sodium hydroxide, potassium hydroxide and the like. The oxides of alkaline metals may also be used, for example, calcium oxide and magnesium oxide. The oils are stabilized by dispersing a small proportion of the alkaline materials therein. The preferred amounts of the alkali metal salts, including magnesium salts, of volatile organic acids range from 0.1 to 0.5%; however, larger amounts up to 3% may be used. The alkali metal hydroxides may be added in the same proportions. The alkaline oxides, such as calcium oxide or magnesium oxide are more effective when added in proportions of 2 to 3.5%, however, smaller proportions may be used. These alkaline materials may be used in any lubricating oil such as hydrogenated hydrocarbon oils, hydrogenated lubricating oils, and, in general, in mineral oils having a Saybolt viscosity of 50 sec. and above at 210° F.

A dispersion of these alkaline materials in oil may be prepared by one of several methods. However, we have found that these alkaline materials can be dissolved in a suitable volatile solvent, dispersed in the hot oil by agitation or some suitable method and then flashed; thereby leaving the dry alkaline material dispersed in the oil.

Figure 3 of the attached drawings discloses a plan view, partly in section, of an apparatus for dispersing the alkaline materials in the oil by the above method. The oil to be stabilized is withdrawn from the storage tank 10 by the pump 11 through the conduit 12 and passed under pressure through the heater or pipe still 13. The oil may be heated to any desired temperature, depending upon the solvent used for the alkaline material. In this particular example, the oil was heated to 300° F. at about 50 to 75 pounds per square inch pressures. It should be understood that higher or lower temperatures and pressures may be used. For example, the temperatures may range from 150° F. to 1000° F. and the pressure may range from 50 to 350 pounds per sq. inch. The hot oil is then passed through the conduit 14 to the mixer 15 and a small quantity of an aqueous solution and/or suspension of sodium carbonate, or any of the alkaline materials, is introduced into the mixer by the pump 16 and conduit 17. Diagonally disposed perforated baffles 18 are placed in the mixer to insure thorough contact and agitation of the oil and solution. The mixture or dispersed solution of alkaline material in the oil is then passed through the conduit 19, reducing valve 20 and introduced into the low pressure or atmospheric flash drum 21. At the low pressure and high temperature prevailing in the flash drum, the water or solvent vaporizes and passes off through the vent 22. When desired, the vent 22 may be provided with a valve to flash the solvent; this is particularly true when the oil is under high pressure and temperature. A baffle 23, or baffles, may be disposed near the vent outlet to separate the droplets of oil that may be occluded in the steam or volatile solvent. After the water or solvent has been flashed, the alkaline material remains dispersed or suspended throughout the body of oil. The oil is then withdrawn through the valved conduit 24 and passed through the cooler 25. A suitable cooling medium is passed through the cooler by the lines 26 and 27. In fact, the solution of alkaline material to be dispersed or colloidally suspended in the oil may be heated by being passed in heat exchange relation with the cooler 25 before being introduced into the mixer 15. The cooled oil containing the dispersed sodium carbonate or alkaline material is then passed through the conduit 28 to the storage tank 29.

Instead of using the mixer 15, as set forth hereinabove, for preparing a dispersion of the alkaline solution in the oil, any type of suitable dispersing means may be used, for example, a colloidal mill. Also it should be understood that other volatile solvents, such as alcohol and ether, may be used for the alkaline materials soluble therein, for example, sodium hydroxide or potassium hydroxide may be dissolved in alcohol. Furthermore, the amount of solution added to the oil should be adjusted so that the resulting oil will contain from 0.1 to 3.5% of the dispersed alkaline material.

The following table illustrates the effectiveness of the herein described alkaline materials for inhibiting color and sludge formations in mineral oils. The following data are based upon a lubricating oil which has a Saybolt viscosity of about 92 seconds at 100° F. and about 1800 seconds at 210° F. and an initial true color of 25. The sludging time was determined by the method set forth hereinbefore in connection with Figure 1, except the oil was heated to 340° F.

Table

Stabilizer	Percent of stabilizer added	True color of the oil after		Sludging time	
		15 hrs.	23.5 hrs.	10 mg.	100 mg.
				Hours	*Hours*
Control		1435	2000	29	44
Sodium carbonate	0.2	590	740	56	71
Potassium hydrox	0.3	780		32	47
Potassium carbon	0.2	665		39	50
Calcium oxide	3.0	270	500	44	78
Sodium formate	0.2	598	997	38	50
Sodium hydroxide	3.0	103	197 (63 hrs.)	65	

From the above table it is apparent that the alkali metal salts of volatile organic acids are effective agents for reducing color and sludge formation. Also the alkali metal hydroxides are very effective for this same purpose. Alkaline earth metal oxides are also effective when used in relatively large amounts, that is, up to about three percent. The above alkaline materials also retard the increase in viscosity and inhibit the sludging of the oil and gumming of the metal parts to be lubricated. Of the metal salts we prefer to use the alkali metal salts of volatile or-

ganic acids that dissociate at temperatures below about 400° F.

Attempts have been made to stabilize mineral oils with the alkali metal salts of high molecular weight organic acids, such as sodium stearate, but such compounds have proven to be completely inoperative, whereas, the alkali metal salts of the volatile organic acids, particularly the mono carboxylic acids containing two, three and four carbon atoms, have proved to possess unique properties for this purpose. When 0.2% of sodium stearate was added to the control sample of oil set forth in Tables, the true color of the oil was 2230 after 23.5 hours, and 28 and 42 hours were required to form 10 and 100 milligrams of sludge respectively.

The alkaline materials herein used are not reducing agents and their action cannot be explained by the theory upon which the action of antioxidants is explained. However, it is thought that the deterioration of mineral oils is accompanied by the formation of intermediate acidic products, and the alkaline materials herein described retard the formation of these intermediate acidic products and thereby stabilize the mineral oils against deterioration. The volatile organic acid salts are particularly suitable for this purpose because after the salts have reacted with the intermediate acidic substances formed in the oil, the organic acids evaporate and do not enter into secondary reactions.

While we have described our invention with reference to certain oils and compound, the scope of our invention is not limited thereby except insofar as set forth in the appended claims.

We claim:

1. The process of stabilizing hydrocarbon oils against sludge and color formation which comprises, heating said oil under pressure, mixing with said heated oil a solution of a sludge-inhibiting alkaline metal carbonate, flashing said mixture of oil and solution whereby the solvent is evaporated and the alkaline metal carbonate is colloidally dispersed in said coil.

2. The process of stabilizing refined hydrocarbon mineral oils against sludge and color formation which comprises, dispersing in said oil not more than 3% of an alkali metal carbonate.

3. The process of stabilizing refined hydrocarbon lubricating oils against sludge and color formation which comprises, dispersing in said oil an alkali metal salt of a volatile organic acid selected from the group consisting of sodium carbonate, potassium carbonate, and magnesium carbonate.

4. The process of stabilizing refined hydrocarbon lubricating oils against sludge formation at temperatures of the order of 340° F., which comprises dispersing in said oil an alkaline material selected from the group consisting of sodium carbonate, potassium carbonate and magnesium carbonate; the amount of said carbonate being within the range of 0.1 to 3.5%.

5. The process of stabilizing refined hydrocarbon mineral oils against sludge formation, which comprises heating said oil under pressure to a temperature above 300° F., mixing an aqueous solution of sodium carbonate with said heated oil; flashing the mixture of oil and aqueous solution whereby the solvent is evaporated and the sodium carbonate is colloidally dispersed in said oil.

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