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PLUG FOR REMOVING PARAFFIN ACCUMULATING IN OIL CONDUITS

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This invention relates generally to the removal of paraffin from production tubing, surface flow lines, and other conduits through which oil passes, and particularly to slowly soluble or disintegrable plugs adapted to be passed there-
through for removing paraffin deposits from the walls thereof.

In co-pending application, Serial No. 137,478, filed January 7, 1950, by Harrell L. Bilhartz, Howard E. Greenwell, and Lawrence E. Davis, now Patent No. 2,603,804, said Bilhartz and Greenwell being co-inventors of the present invention, there is disclosed a paraffin-removing plug consisting of an oil-soluble base material and a rosin amine salt of an organic acid. The purpose of the invention disclosed therein was to provide slowly soluble or disintegrable plugs adapted to be passed through production tubing, surface flow lines, and other conduits through which oil flows thereby to remove, by cutting or scraping, paraffin deposited on the walls thereof.

While the plugs disclosed in said application have proved to be generally satisfactory, the present invention provides a plug of the same general type but which has greater physical strength and ability to resist shattering. It has been found that the physical properties of oil soluble plugs can be materially improved by including in the composition thereof at least a minor quantity of an oil-soluble cellulose ether.

Accordingly, one object of the present invention is to provide an oil-soluble paraffin-removing plug of improved strength and resistance to shattering during passage through production tubing, surface flow lines and other conduits through which oil flows.

Another object is to provide a paraffin-removing plug which is slowly soluble in oil, which is adapted to be passed through conduits through which oil flows to remove paraffin deposited on the walls thereof, and which has sufficient physical strength to resist shattering or breaking during normal handling in storage and in use.

Other objects and features of the invention will be apparent from the description which follows.

In accordance with this invention, there is provided an oil-soluble plug which is adapted to be passed through production tubing, surface flow lines, or other oil conduits, and which comprises a slowly soluble or disintegrable base material, a rosin amine salt of an organic acid, and a small proportion of an oil soluble cellulose ether. The plug is formed so as to fit snugly in the conduit through which it is caused to be propelled by

applying fluid pressure on one end thereof. In order for the plug to effectively remove paraffin, it is necessary for it to be sufficiently hard that the forward end provides a cutting surface that will scrape or cut the paraffin upon contact therewith, to maintain shape and remain hard at temperatures in excess of the highest temperature expected to be encountered in temporary storage places, that is, in excess of approximately 150° F., to dissolve or disintegrate in the oil flowing through the conduit within a desired period of time, such as, for example, from one hour to a day or more after passing through the conduit and removing the paraffin from the interior thereof, and to be free from shattering or breaking under pressures required for propelling the plug through the production tubing or flow line. This is accomplished in accordance with the invention by varying the percentages of the above mentioned components of the plug, dependent upon the conditions in each particular case.

The base materials may be exemplified by high melting point waxes, such as microcrystalline hydrocarbon waxes derived from petroleum and having melting points between 150° F. and 200° F.; ceresin; montan wax; chloro-waxes; waxes from the Fischer-Tropsch process; waxes from crude oil tank bottoms; high melting synthetic wax-like materials such as the anilides and amides of the higher fatty acids; ester gums; high melting petroleum resins derived from crude oil residues by solvent treatment and/or oxidation; petroleum asphalts having softening points (R. & B.) between 200° F. and 300° F. and having a maximum penetration at 77° F. of 10, and preferably between 5 and 10; waxy asphalts derived from petroleum residuum by propane treatment; oxidized residues from thermal or catalytic oil cracking units; and residues from coal tar, coal tar pitch, and vegetable pitches; or mixture of two or more of these materials.

The rosin amines used for the production of the rosin amine salts included as a component of the plug may be prepared from dehydrogenated rosin, disproportionated rosin, or hydrogenated rosin by first reacting with ammonia to form the nitrile and then hydrogenating the nitrile to the amine. The step of making the nitrile may be carried out by passing gaseous ammonia into the molten rosin material and vaporizing the water as fast as it is formed or by heating the rosin material and ammonia in the presence of a dehydration catalyst. The nitrile is preferably purified by alkali extraction or by distillation to remove unconverted acids

prior to hydrogenation to the amine, since the acidic materials frequently destroy the activity of the hydrogenation catalyst. The hydrogenation of the nitrile may be carried out in the presence or absence of a solvent and in the presence or absence of ammonia. The catalyst may be any of the well-known hydrogenation catalysts such as Raney nickel, Raney cobalt, activated nickel, cobalt, palladium or platinum, etc., and supports may be used if desired. The hydrogenation is usually carried out under a pressure of about 200 to about 8,000 pounds per square inch at a temperature of about 20° C. to about 200° C.

The rosin amine salts which may be used in accordance with this invention include the salts of organic acids such as the higher fatty acids, for example, lauric, stearic, and palmitic acids; naphthenic acids having a molecular weight preferably between 170 and 350; sulfonic acids derived by the treatment of petroleum fractions with sulfuric acid or other sulfonating agents. Of these, the oil-soluble sulfonic acids obtained as a by-product in the manufacture of mineral white oils are preferred, and these acids usually have a molecular weight between 400 and 550 and acid numbers between 80 and 140 mg. KOH per gram. Sulfonic acids derived from higher alkyl benzenes, naphthalenes, and anthracenes may also be used, as well as carboxylic acids such as abietic acid, and acids from the oxidation of paraffin wax. Particularly suitable are the rosin amine salts of stearic acid, palmitic acid, and naphthenic acid. The rosin amine salts may be prepared simply by mixing the amine with an equivalent amount of organic acid and heating, or by dissolving the amine and acid in a suitable solvent, heating if necessary, and then removing the solvent.

The cellulose ether employed as a component of the plugs made in accordance with this invention may be any oil-soluble cellulose ether such, for example, as ethyl, propyl, isopropyl, n-butyl, isobutyl, or benzyl cellulose. Some of these cellulose ethers are commercially available, and various processes are known for the preparation thereof. Thus, cellulose may be treated with a base, for example sodium hydroxide, to form alkali cellulose which is then heated with the appropriate alkyl halide or alkyl sulfate. A method more recently employed for preparation of cellulose ethers involves dissolving cellulose in a quaternary ammonium hydroxide and then treating the cellulose with a desired dialkyl sulfate or alkyl halide. Ethyl cellulose has been found to be especially suitable for use in the present invention.

Oil-soluble cellulose ethers, such as ethyl cellulose, have been found to be incompatible with asphalts, paraffin base waxes, and certain other waxes useful as components of oil-soluble paraffin removing plugs, and therefore may not be readily mixed therewith. It has been found, however, that the oil-soluble cellulose ethers may be readily mixed with the incompatible asphalt or wax base materials by first dissolving the cellulose ether in a substance which is compatible both with the cellulose ether and with the base material to form a mixture which shall hereinafter be referred to as a "cellulose ether solution." The cellulose ether solution may then be mixed immediately with the other components to form a homogeneous mass from which the plugs may be shaped, or may be cooled and stored until

ready for use, at which time it may be reheated to a melting temperature.

There are several substances which are mutually compatible with the oil-soluble cellulose ethers and with the other components of the paraffin-removing plug, and which are therefore suitable for forming the cellulose ether solution. For example, beeswax, montan wax, stearic acid, phenolic resin, castor oil, or dibutyl phthalate may be used for this purpose. The oil-soluble cellulose ether solution may be made by heating montan wax to a temperature of approximately 250° F. and slowly adding thereto as much oil-soluble cellulose ether as will readily dissolve therein, adding also a very small quantity of an anti-oxidant, such as diamylphenol, which serves the purpose of preventing oxidation of the cellulose ether when exposed to the high temperature required for melting the montan wax and dissolving the cellulose ether therein. Although it will be understood that the percentages of the several components of the solution are not critical, a satisfactory solution has been found to be one consisting of 87 parts montan wax to 12 parts of ethyl cellulose and one part of diamylphenol.

Oil-soluble paraffin removing plugs, according to this invention, may be made by melting the base material, the rosin amine salt, if necessary, and the cellulose ether or cellulose ether solution, depending on the base material employed, mixing these components in the desired proportions, and shaping the molten or plastic material to the desired contour and dimensions by molding or extrusion. The relative percentages of the components of the plugs may be varied considerably, depending upon the conditions under which they are to be used. In general, the oil-soluble base material comprising wax or asphalt may constitute from about 90% to about 55% of the total weight of the plug, the rosin amine salt of an organic acid may comprise from about 5% to about 45% of the total weight, while the amount of oil-soluble cellulose ether or cellulose ether solution employed may preferably be that which is required to incorporate into the plugs from about 0.5% to about 5% by weight of the oil-soluble cellulose ether. While the percentage of cellulose ether employed in the plug may be increased considerably over the suggested 5%, little, if any, improvement in the physical properties of the plugs is noted by the inclusion of a greater amount of this material.

The following examples are illustrative of plugs which will satisfactorily remove paraffin under the various conditions indicated, which are sufficiently oil soluble to dissolve in oil within a period of several hours, which have sufficient physical strength to resist shattering or breakage during normally expected conditions of storage and use, and which will retain their physical shape and remain hard at the highest temperatures expected to be encountered in temporary storage places.

Example I

A plug composed of 85% by weight of asphalt with a melting point between 230° F. and 240° F. determined by ASTM ring and ball method and a penetration from 7 to 10, 10% by weight of rosin amine stearate, and 5% by weight of an ethyl cellulose solution comprising 87 parts montan wax, 12 parts ethyl cellulose, and one part diamylphenol was found to have physical characteristics making it suitable for use in removing

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paraffin deposits from the interior of an oil flow line at temperatures in the range of 120° F. to 125° F. A plug of this composition immersed in a typical crude oil at a temperature of approximately 110° F. was found to dissolve to about half its weight in one hour. When a plug of this composition one inch in diameter and 1½ inches long was subjected to the shock imposed thereon by dropping of a 621 gram weight from a height of 32 inches, said plug showed only a very slight crack on one edge which did not substantially decrease the paraffin-removing properties of the plug.

Example II

For removing paraffin deposits from oil lines at temperatures less than about 100° F., a suitable plug may be made consisting of 90% by weight of the same asphalt as employed in Example I, 5% by weight of rosin amine stearate, and 5% by weight of the same cellulose ether solution as employed in Example I. A plug of this composition subjected to the same shock test as described in connection with Example I was found to develop only a minor edge fracture.

Example III

A plug composed of 55% by weight of microcrystalline wax having a melting point between 190° F. and 195° F., 40% rosin amine stearate, and 5% of the same cellulose ether solution as employed in Example I will effectively remove paraffin deposits from the interior of an oil flow line and completely dissolve in the oil within a period of several hours at a temperature of approximately 130° F.

Example IV

Plugs composed of 50% of the same asphalt as employed in Example I, 35% microcrystalline wax, 10% rosin amine stearate, and 5% of the same cellulose ether solution as used in Example I will effectively remove paraffin deposits and dissolve at a satisfactory rate in a surface oil line at temperatures between 80° F. and 100° F.

Plugs provided in accordance with this invention are satisfactory for removing paraffin deposits from any production tubing or other conduit through which oil flows. In the actual operation of scraping or cutting paraffin from the interior of such oil flow lines, the procedure is not one of using a plug of given percentages of base material such as wax or asphalt, or mixtures thereof, with the rosin amine salt and cellulose ether solution, but instead the percentages of such materials are varied to obtain, under the conditions of each case where it is desired to remove paraffin deposits, a plug having the aforementioned necessary characteristics, that is, sufficiently hard to provide an effective cutting surface, maintain shape and remain hard at temperatures in excess of those expected to be encountered in temporary storage places, sufficiently soluble to dissolve in oil within a desired period of time, and will not shatter or break under the compression forces necessary to propel the plug through the conduit. This will be apparent when consideration is given to the fact from location to location there are variations in the temperatures encountered in the oil flow lines, the composition of the oil in which the soluble plug is required to dissolve, the time in which it is desirable that the plug dissolve, the amount of paraffin deposited and other factors, which need not be mentioned. Field tests

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have indicated, for example, that the wax content may vary from 0% to 55% by weight, asphalt content from 0% to 90%, rosin amine salt from 5% to 45%, and the cellulose ether solution sufficient to incorporate into the plugs from about 0.5% to 5% of cellulose ether, dependent upon the particular conditions encountered.

It is to be noted that plugs may be provided preferably in accordance with this invention containing either asphalt alone, or wax alone as the base materials, or mixtures thereof. It is necessary in each case, however, to include at least 5% by weight of the rosin amine salt and sufficient cellulose ether solution to provide at least about 0.5% oil-soluble cellulose ether in order to obtain the desired physical properties of the plug.

In the practice of the invention, a plug is formed by varying the percentages of the components until the necessary physical properties are obtained for the conditions under which the plug is to be employed. The plug is shaped to conform with the interior of the oil conduit and is adapted to fit snugly therein. The plug is then inserted in the conduit and oil under pressure is applied to one end thereof causing the plug to be propelled through the conduit, thereby removing paraffin deposits. While moving through the conduit and also after traveling to the end of the conduit with removal of all the paraffin deposited on the interior thereof, the plug will dissolve relatively slowly in the oil.

While a number of embodiments have been described above, it will be understood that this invention is susceptible of various other embodiments within the scope of the appended claims. For example, the plugs may comprise solid, cylindrical shapes, or in the event that more rapid dissolution or disintegration is required, the plugs may be formed as hollow cylinders having one end closed so that the internal surface of the plug may be subjected to the solvent action of the oil in the conduit being cleaned. If necessary, the hollow, cylindrical plugs may be formed with internal webs to give added strength, or the leading end of the plug, be it either solid or hollow, may be recessed or dished rather than flat.

We claim:

1. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble base material, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of an oil-soluble cellulose ether.
2. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of asphalt, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of an oil-soluble cellulose ether.
3. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble wax, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids,

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naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of an oil-soluble cellulose ether.

4. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble base material consisting of asphalt and wax, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of an oil-soluble cellulose ether.

5. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble base material, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of ethyl cellulose.

6. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of asphalt, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic

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acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of ethyl cellulose.

7. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble wax, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of ethyl cellulose.

8. A plug for removing paraffin from the wall of a conduit through which oil flows, including between 55% and 90% by weight of an oil-soluble base material consisting of asphalt and wax, between 5% and 45% by weight of a rosin amine salt of an organic acid selected from the group comprising the higher fatty acids, naphthenic acids, sulfonic acids, carboxylic acids, and acids derived from the oxidation of paraffin wax, and between 0.5% and 5% by weight of ethyl cellulose.

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