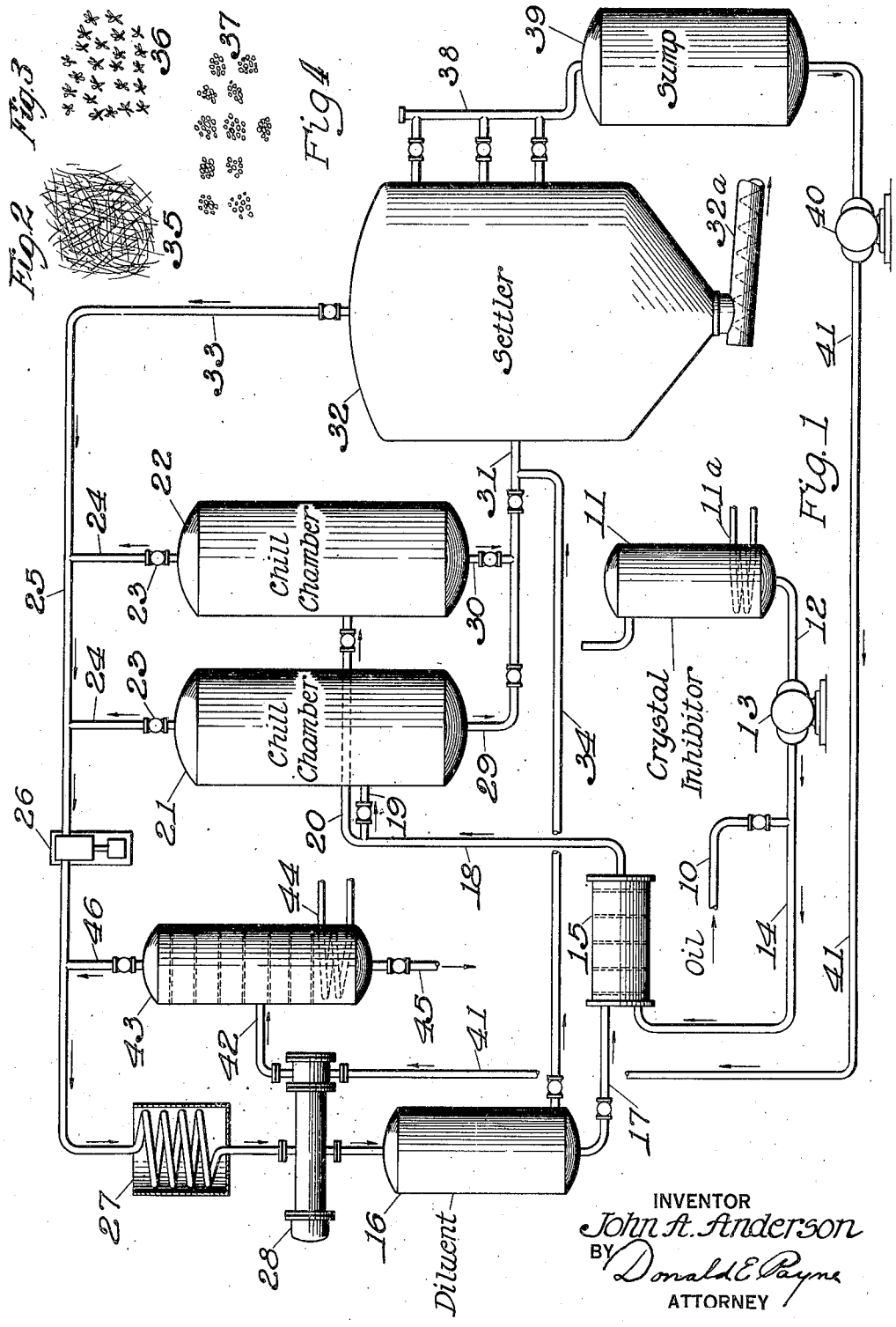
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DEWAXING PROCESS

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DEWAXING PROCESS

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This invention relates to the separation of wax from mineral oil distillate stock and it pertains more particularly to a method of congealing wax in such a manner that it may be readily separated from oil-propane mixtures by cold settling. The modern trend in the manufacture of lubricating oils is to use overhead or distillate oils, even for the heavy grades, instead of using residual oils or blends of residual with distillate oils. Overhead or distillate lubricating stocks contain mixtures of paraffin and petrolatum waxes which must be removed if the finished lubricant is to have a low pour point. The object of my invention is to provide a simple and economical method and means for separating such wax from distillate lubricating stocks.

One of the newer methods of removing wax from oils consists in diluting the waxy oil with a liquefied hydrocarbon gas such as propane. Certain waxes can be cold settled from such a solution, but many other waxes will not settle at all, or at least will not settle sufficiently to make the process commercially feasible. It appears that, because of the low viscosity of propane, certain factors operate to cause the growth of large wax crystals, and if there is a large amount of paraffin wax present the wax crystals will not settle to form a dense cake but will be held apart by a skeleton structure of interlacing crystals. This formation of large paraffin crystals is one of the important characteristics of propane dewaxing, and although many distillate stocks can be readily settled, I have found that settling rates may be markedly increased, that denser wax cakes may be produced, that greater oil yields may be obtained and that a more satisfactory process generally will result from the use of crystallization regulators of the type hereinafter defined.

Many of the crystallization regulators which I may use are of relatively no value when used in cold settling from naphtha but are extremely helpful in settling from propane solutions. Furthermore, many substances of this class remain in the oil after the dewaxing step when ordinary hydrocarbon diluents are used, and large amounts must be continuously used up in the settling process. I have found that propane precipitates substantially all of these crystallization regulator substances from the oil so that they may be recovered from the wax and reused over and over again. This not only effects a saving in the cost of the inhibitor but it avoids the contamination and discolorization of the finished oils and saves the expense of further treating and decolorizing.

Heretofore distillate stocks have not been considered amenable to settling, which is probably the least expensive and the simplest of all dewaxing processes. Some settling may be obtained from propane when this liquefied normally gaseous diluent is employed instead of naphtha, but the oil yields are not sufficient to make the process commercially feasible. By employing wax crystallization regulator substances in combination with the propane diluent I have accomplished what has heretofore been considered impossible, namely, the commercial separation of paraffin wax from oil by cold settling, using reasonable amounts of diluent and obtaining high settling rates, low bottoms and high yields of low pour point oil.

I have found that if my diluted waxy oil is chilled and allowed to settle in a tank 100 units deep, the wax will settle to a distance of eight or ten units from the bottom or, in other words, I will obtain 8–10% bottoms and 92–90% of wax-free diluted oil. The particular yields will depend largely on the nature of waxy distillate stock employed, the amount of diluent used, the nature and quantity of crystallization regulators employed, and the general manipulation of the process.

As crystallization regulators in this process I may use naphthenic or aromatic hydrocarbons with long paraffine side chains. Such compounds may occur in small quantities in certain crude petroleum residues, such as Smackover, Winkler and Mid-Continent residuums, and they may be separated therefrom by precipitating reduced crudes with propane, the sustances being chiefly segregated in the precipitated portions. These naphthenic or aromatic compounds with long paraffin side chains may also be synthetically prepared by condensing chlorinated paraffin oils or waxes with naphthalene or other similar product in the presence of aluminum chloride or equivalent catalyst. Some of these synthetic substances may contain chlorine in unstable form and may therefore be unsafe as pour point depressors in lubricating oils; nevertheless, I have found that they are excellent crystallization regulators or settling promoters when used in a propane dewaxing system, and I have further found that since these substances are precipitated with the wax from the propane solution it is immaterial whether or not they contain loosely bound chlorine, as the finished oil is not contaminated by the crystallization regulating material.

Another type of crystallization regulator comprises the class of metal soaps, particularly aluminum stearate. I have obtained very satis-

factory results with iron stearate, calcium stearate, etc.; also palmitic and hydrogenated fatty acid soaps of aluminum, calcium, copper, zinc, etc. In general the fatty acid oil-soluble soaps of metals such as sodium aluminum, iron, calcium, zinc, etc. are effective. These soaps may be used in proportions of about 0.05 to 0.5%, and in some cases a little more or a little less soap may be used than these figures would indicate. I have found that these soaps, particularly the stearates, will decrease the bottoms by as much as 25 to 35%. Soaps of organic amines may also be used, e. g., triethanolamine oleate.

A third class of substances which I may use to control the crystallization regulator is that of the oil-soluble polymerized resins or rubber hydrocarbons. Rubber may be introduced as latex followed by dehydration. Hydrogenated rubber may be employed instead of raw rubber latex. Instead of natural rubber latex I may employ similar compounds which are prepared synthetically by polymerization or otherwise.

All of these various classes of compounds have the effect of regulating crystal formation of paraffin wax when this wax is chilled in a propane-oil solution. Instead of crystallizing in large plates or needles which cannot be compacted, which entrain large amounts of oil and which yield a voluminous wax cake, the paraffin wax separates out in small aggregates in the form of compact particles which rapidly settle to form a dense cake and which therefore make it possible to effect the removal of paraffin wax by settling. Also, in filtration, such wax forms a more compact cake on the filter leaves and gives higher filter rates, higher yields and denser wax cakes.

My invention will be more clearly understood by referring to the accompanying drawing which forms a part of this specification, and in which—

Figure 1 represents a diagrammatic plan of my improved process, and

Figure 2 represents the crystal formation of wax particles solidified without the use of my wax-separation aids.

Figs. 3 and 4 represent the agglomerated wax structure brought about by my wax-separation aids.

As a diluent in my process I prefer to use propane, but it should be understood that I may employ other liquefied normally gaseous hydrocarbons or mixtures thereof, whether saturated or unsaturated. For instance, I may use commercial propane which contains large amounts of isobutane and small amounts of butane, ethane, propylene, etc. In some cases the invention may also be applicable to the use of other liquefied normally gaseous diluents, such as methyl ether, methyl chloride, dimethylamine, etc. Some of my crystallization regulators are also useful in processes which employ light gasoline, petroleum ether, etc. as the diluent.

The invention will be described in connection with the dewaxing of Mid-Continent untreated distillate having a viscosity of about 60 seconds Saybolt at 210° F. The invention, however, is equally applicable to other distillate stocks, treated or untreated, including even paraffin distillate.

The distillate lubricating oil stock is introduced from a suitable storage tank (not shown) through line **10**, and it is mixed with about one percent of the crystallization regulators from storage **11**, the reagent (which is dissolved in a small amount of oil or heated to about 100–150° F. by steam coils **11a**) being withdrawn through pipe **12** by proportioning pump **13** and mixed with the oil in pipe **14** and mixer **15**. Propane from storage tank **16** is admitted through line **17** to mixer **15**, a suitable pump being employed, if necessary,—the volume of propane being preferably six or eight times the volume of distillate stock. In mixer **15** the oil is dissolved in the propane and, if desired, a steam coil may be employed to effect complete solution of the stock therein. The propane solution is then passed through pipe **18** and pipes **19** or **20** to chill chambers **21** or **22**. Refrigeration is effected by removing propane vapors through valves **23**, pipes **24** and line **25** by means of compressor **26**, the vapors being liquefied in condenser **27** and returned through heat exchanger **28** to diluent storage tank **16**. When the pressure in the respective chill chamber is reduced to about zero pounds gauge and the temperature of the propane mixture is about —40° F., the slurry is passed through pipes **29** or **30** and pipes **31** to continuous settler **32**. The temperature may be maintained at low level in the settler by removing propane vapors through pipes **33**. Instead of using separate chill chambers I may use a continuous chiller, the slurry being passed through an elongated conduit and vapors being removed at intervals along its length. If additional propane is required in the chillers it may be introduced through pipe **34**.

The rapidity with which the wax crystals settle out in settler **32** will depend to a large extent upon the nature of the waxy oil, the nature of the diluent and the amount and efficiency of the crystallization regulator. If the Mid-Continent stock above described is chilled in the absence of a settling aid the wax will crystallize in the form of needles or plates **35** as shown in Figure 2. By using effective settling agents the wax assumes the form of star-shaped aggregates **36** or rounded particles **37** (see Figure 2) which settle rapidly and to very low bottoms and which give a dense wax cake.

The clear oil is decanted from the settling tank through pipe **38** and wax slurry is continuously removed at the bottom through wax screw **32a** to suitable diluent recovery means. The wax may be washed several times with propane or reprecipitated (repulped),—such expedients being familiar to those skilled in the art. The cold wax-free diluted oil may be collected in a suitable sump or receiver **39** and then passed by means of pump **40** through pipe **41** to exchanger **28** wherein it absorbs the heat from liquefied propane. The warm mixture is then passed by pipe **42** to stripping still **43** equipped with steam coil **44**, the finished oil being withdrawn through pipe **45** and propane being returned by pipe **46** and condenser **27** to storage **16**.

While I have disclosed a preferred embodiment of my invention it should be understood that I do not limit myself to any of the details hereinabove set forth. The important feature of my invention is the combination of propane settling with a crystallization regulator as hereinabove described. The substance may, in the case of naphthenic or aromatic compounds with long side chains, be used in proportions of about one-tenth percent to two percent of the waxy oil stock,—preferably about 0.5%. When soaps are used, the amounts may be somewhat smaller, usually about .05% to .5%. When hydrogenated rubber or similar resin is employed I use about one-half to one percent of the waxy oil stock.

I have found that many substances which are generally referred to as pour point depressors are effective because of their tendency to control wax crystallization and form rounded wax particles instead of needles or plates. It is apparent, of course, that I may employ any of these pour point depressors as crystallization regulators in my propane settling or filtering processes.

Other modifications of my invention will be apparent to those skilled in the art, and while I have described the invention in detail, it should be understood that I do not limit myself to any of the details except as defined by the following claims which should be construed as broadly as the prior art will permit.

I claim:

1. The method of separating wax which tends to solidify in crystalline form from wax containing oil, comprises adding thereto a small amount of a triethanolamine soap, dissolving said oil-wax soap mixture in liquid propane, chilling the propane solution to effect the solidification of wax in the form of agglomerated particles, mechanically separating the solidified wax from the diluted oil, and removing propane from the separated wax and oil.

2. The method of claim 1 wherein the soap is triethanolamine oleate and is present in amounts from about .05 to 0.5%.

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