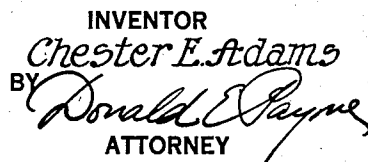


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WAX RECOVERY

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This invention relates to the refining of wax bearing mineral oils, and it pertains more particularly to the dewaxing of paraffin distillates or other stocks containing sweatable wax by the use of crystallization regulators, the dewaxing being effected by means of propane and the crystallization regulator being recovered for reuse.

Propane dewaxing has offered many new and unexpected advantages in the art of preparing low pour point lubricating oils from heavy distillate stocks and the like containing mixtures of paraffin and petrolatum waxes which are difficult to remove by other processes. The propane has not only afforded a means for obtaining direct refrigeration, for lowering the refrigeration costs, and for increasing cooling rates from a few degrees per hour to several degrees per minute, but it has shown remarkable and unexpected results as a diluent. The propane diluent causes the crystallization of wax mixtures in filterable and settleable form, increases filtering and settling rates to a remarkable degree, and does not dissolve even as much wax as light gasoline. The propane dewaxing system for obtaining low pour point lubricating oils (from about 60 to 110 seconds Saybolt viscosity at 210° F.) has proven to be extremely successful on a commercial scale and has been found to offer an unsurpassed flexibility and economy of operation. The object of the present invention is to extend the scope of this propane dewaxing process to lighter oils, the so-called paraffin distillates, and to combine propane dewaxing with a wax-sweating operation so that wax of a desired melting point can be obtained from the process as well as dewaxed oils.

A further object of my invention is to provide a means for obtaining an extremely rapid separation of sweatable wax from paraffin distillate and the like. A further object is to obtain dense, dry wax cakes which contain minimum amounts of oil and which will not have to be washed with propane or deoiled prior to sweating. A further object is to increase the amount of salable wax that can be obtained from a given paraffin distillate and to improve the value of the dewaxed oil. A further object is to avoid the necessity of continuously supplying crystallization regulators or pour point depressors which are expensive and which might otherwise detract from the commercial success of the process. A further object is to simplify the dewaxing of paraffin distillate and the apparatus therefor, to dewax such distillates continuously, and to decrease the costs of equipment and operating expense. Other ob-

jects will be apparent from the following detailed description of the invention:

This invention is particularly applicable to a different type of oil than is generally used for the crankcase lubrication of automobile engines. It specifically relates to "paraffin distillates" or stocks containing sweatable wax, a preferred example being a fraction of Mid-Continent crude between 62% and 74% distilled,—this fraction having a viscosity of about 136 seconds Saybolt at 100° F., a gravity of about 27.8 A. P. I. and a wax content of about 10.4% (determined by a 50-50 acetone-benzol mixture at 10° F.). Heretofore it has been common practice to merely chill such distillates and press them in Carbondale presses, the chilling often requiring several hours and the filtering or pressing requiring a like amount of time. I dilute the waxy stock with a limited amount of propane, add a small amount of a crystallization regulator, chill by vaporizing some of the propane, leaving or adding enough propane to insure about 35% to 50% for use as diluent, and I finally filter the wax from the oil on a continuous filter. The cooling may be effected in ten or fifteen minutes and the filtering may be effected in from three to ten minutes. The crystallization regulator appears to prevent interlacing of wax crystals and consequent entrainment of unduly large amounts of oil, and by using such materials I can obtain a very dry, dense wax cake which does not have to be washed or de-oiled and which, after the removal of propane, may be readily sweated. In previous propane dewaxing processes it has been necessary to use much larger amounts of propane of the order of 75-80%, in order to obtain satisfactory filter rates. By the use of a continuous filter and a crystallization regulator, I have been able to reduce the amount of propane in the mixture and still obtain as good or even higher filter rates, but with the advantage of more complete wax removal for a given filtering temperature because of the smaller amount of diluent in the mixture.

I have discovered that practically all of the crystallization regulator is separated from the diluted oil with the wax mixture, that it has no undesirable effects in the sweating operation and that in fact it appears to increase the yield of recoverable wax of a given melting point. I have further discovered that the crystallization regulator is not combined with the high melting wax but that after the sweating operation it is concentrated almost entirely in the drips or foots oil, it may be recovered for reuse by distillation of the drips or foots oil, or this oil may be re-

turned to the dewaxing step with the crystallization regulator admixed therewith.

The accompanying drawing which forms a part of this specification diagrammatically represents an elevational plan of my improved system, parts of the apparatus being broken away and parts shown in section.

I will describe my invention as applied to the recovery of wax from 136 sec. viscosity (Saybolt 100° F.) pipe still paraffin distillate from Mid-Continent crude, but it should be understood that the invention is applicable to any other oil containing sweatable wax. As a crystallization regulator I prefer to use Pourerex, which is a product made as follows: 180 parts by weight of chlorinated wax (130° F. melting point paraffin wax chlorinated to 13% chlorine content) are heated with 20 parts by weight of naphthalene to a temperature of 300° F.; two to four parts by weight of aluminum chloride are gradually introduced into this mixture the addition requiring only a few minutes. The mixture is stirred and maintained at a temperature of about 300° F. for a period of about 2 to 20 minutes, preferably about 10 minutes. The hot products are then separated from the granular sludge by filtration and/or by gravity, and the reaction products are neutralized with hot caustic soda to completely remove all uncombined and loosely bound chlorine, hydrochloric acid, etc. The neutralized products are washed with water and are then ready for use. The product prepared in this manner is designated by the trade mark "Pourerex" and is my preferred crystallization regulator. I may, however, employ the substance which is made in accordance with Davis Patent 1,815,022 and commercially known by the trade mark "Paraflo". I may also use highly refined pitch still residues or gum fractions, residues from the distillation of petrolatum, asphaltic residues, soaps, and equivalent substances which have the desirable properties of preventing the interlacing of the wax crystals, and the present invention is not limited to any specific crystallization regulator.

Referring to the drawing, propane from pipe 10, a small amount of Pourerex from pipe 11 and the paraffin distillate from pipe 12 are introduced into mixer 13 which is maintained at a sufficiently high temperature and pressure to effect a homogeneous mixture of the wax, Pourerex and oil in the propane. I employ a sufficient amount of propane to leave about 35% to 50% propane by volume in the chilled slurry which is charged to the filter. The amount of propane introduced through pipe 10 must be sufficient to effect the refrigeration and to compensate for heat absorption, or additional propane or similar refrigerant must be subsequently added. The amount of Pourerex may vary from about .05 to 2.0% based on the oil, but it is preferably about .1% to .2% by weight. The Pourerex may, of course, be introduced in the oil solution and may be dissolved in the incoming oil. The temperature of the mixer is preferably about 80-100° F., the temperature necessarily depending upon the particular type of equipment employed, the volume of propane used, the nature of the oil and wax, the amount of wax in the oil, etc.

The homogeneous solution is introduced from mixer 13 through pipe 14 and valve 15a into chill chamber A. The chill chamber should be warmed to the temperature of the incoming mixture and should be at the same pressure as the incoming mixture so that shock chilling will be avoided.

Valve 17a is closed and valve 18a is opened so that the mixture is refrigerated by removing propane vapors through pipe 19 by means of compressor 20, the compressed propane vapors being condensed in coil 21, and cooled by a cooling medium in box 22. The condensed propane is then introduced into separator 23, air and non-condensable gas being vented from the top thereof through valve 24 and liquid propane being conducted through pipe 25 to propane storage tank 26.

As soon as the propane-oil-wax slurry in chiller A reaches a temperature of about -10° to +10° F., preferably 0° F., valve 18a is closed and the cold slurry is withdrawn through opened valve 17a and pipe 27 by pump 28, which is controlled by a liquid level device 29 in trough 30 in the pressure filter chamber 31. It should be understood, of course, that while the mixture in chamber A is being cooled, chamber B is being filled and chamber C is being emptied,—the arrangement of batch chillers being designed to permit the operation of a continuous filter. I may employ continuous pipe chillers and I may employ a receiver or storage tank to maintain a suitable volume of wax slurry for charging to the filter.

The filter is preferably of the continuous type and is shown in the drawing as a drum with a peripheral canvas or filter element 32, the drum being formed of a plurality of segments 33, 33', etc., each of which is connected to a port in the supporting shaft. The filter shown in the drawing rotates in a clockwise direction, the cake being built up while the segment is immersed in the slurry, being dried as the cake advances out of the slurry, being washed, and finally being discharged, as will be hereinafter described. I may use any type of filter instead of the continuous type described.

The wax-free diluted oil passes through pipe 35 to filtrate storage tank 36, from which it is forced by pump 37 through pipe 38 to steam still 39. This still is heated by steam coil 40 or other suitable means, and propane is vaporized under pressure and conveyed by pipe 41 to condenser coils 21. The hot oil is then passed through pipe 42 and reducing valve 43 into low pressure chamber 44, wherein the last traces of propane are vaporized and removed through pipe 45 to pipe 19 and compressor 20. If desired, I may employ a suitable stripping means for insuring desired flash characteristics of the finished oil which is removed through pipe 46 to a suitable storage tank.

The wax on the filter may be washed with propane which is led into the filter by pipe 47 and sprayed onto the cake by nozzles 48. It should be understood that I may maintain the pressure in the filter by means of an inert gas or a lower boiling gas, such as ethane, and I may employ butane or other solvent instead of propane as a washing liquid.

The wax cake is preferably removed from the filter by a blow-back system, port 49 being connected by pipe 50 to the top of storage tank 26 or to some other source of pressure. Other cake discharge means may, of course, be employed. The wax cake is scraped from bulged filter cloth 51 by scraper 52, and is conveyed by wax screw 53 to a wax melting tank 54, which is heated by steam coils 55. Liberated propane is removed through pipe 56 to propane line 19, and the hot liquid wax is forced by pump 57 to crude wax storage tank 58 from which it is introduced by pipe 59 into sweating oven 60.

It should be understood that any number of sweating ovens may be employed and that they may be of any type or design. The wax is first solidified in the sweating oven by introducing cold water through pipe coil 61, and the temperature is thereafter gradually raised by circulation of warm water through coil 61 to cause the softening and separation from high melting waxes of the so-called "drips" or "foots oil". The drips preferably run to a storage tank (not shown), and from thence they are withdrawn through pipe 62 by pump 63 and forced either through pipe 64 back to mixer 13 to be mixed with incoming oil or through pipe 65 to a suitable storage tank. After the sweating operation the crude scale is melted by steam and withdrawn through suitable pipes not shown.

It will be understood to those skilled in the art that suitable plumbing fixtures, valves, pressure regulators, insulating means, etc. will be supplied when necessary, that a pump 66 will be necessary in propane line 10, etc. I do not limit myself to any of these details except as defined by the appended claims.

Some outstanding features of the invention are: wax can be solidified and filtered in a few minutes while prior art methods require several days; dewaxed oils of much lower pour points can be obtained than were otherwise obtainable; the yield of 120° to 130° melting point waxes from any given crude are markedly increased, and the process is extremely economical in operation. The process is made commercially feasible because of the peculiar and unexpected effect of the crystallization regulator and because this crystallization regulator can be readily recovered for reuse from the drips or foots oil. When Pourrex, Paraflow and the like are employed with paraffin distillates which have been diluted with naphtha, they have little effect, filter rates are not materially increased, and the sweatability of the wax is not improved. However, when Pourrex is used with a propane-diluent, phenomenal results are obtained. A 50-50 mixture of paraffin distillate and propane cooled and filtered in the absence of Pourrex yields only 50% of dewaxed oil; when .03% Pourrex is added to the oil the yield of dewaxed oil is increased to 87.2%. When a 35% propane, 65% paraffin distillate mixture is filtered at about 0° F., the reduced wax cake is 55% of the original oil charge. When 2% of Pourrex is added to the oil the 35:65 mixture gives a wax cake of 19.2% of the original oil charged. When 3% Pourrex is added to the oil in the 35:65 mixture the yield of wax cake is only 12.5%. At the same time the addition of the Pourrex effects a considerable increase in the filter rate; without Pourrex the rate is 10 gallons per square foot per hour, based on the viscous oil charge, and with 3% Pourrex the filter rate is increased to 16.6 gallons per hour. Without Pourrex the thickness of the wax cake is about three-fourths of an inch, and with 2% to 3% of Pourrex the cake is only one-fourth to one-half inch in thickness, illustrating the increased compactness of the wax. Without Pourrex the wax cake is mostly oil and contains only about 15% of wax. With Pourrex the wax content of the filter cake is about 50% to 55%. Without Pourrex the melting point of the reduced wax cake is so low that it cannot readily be determined, and even when 50% propane is used the melting point of the wax cake is only 89° F. When Pourrex is employed the melting point of the wax cake is from 108-114° F. It is significant to note also

that the melting point of the dry wax is several degrees higher when Pourrex is used. In all of these tests the chilling rate can be about 2° to 3½° F. per minute, the filtering temperature about -5° to +5° F., and the filter pressure may be about 15 lbs. per square inch. The filtering rates are very rapid.

The above comparisons of 36:65 propane paraffin distillate mixtures with and without Pourrex are even less striking than the results obtained with 50-50 propane paraffin distillate mixtures. Here again the wax cake, in the absence of Pourrex, is 50% by volume of the oil charged while a wax cake of only about 12½% is obtained by using from .2% to .3% of Pourrex. Quantities of Pourrex larger than 0.3% based on wax-bearing oil are not necessary on this particular stock, but it is found that sweatable wax cakes cannot be obtained with less than .05% of Pourrex.

I have discovered that Pourrex is thrown out of solution with the wax in the chilling step. This is proved by the complete recovery of the Pourrex, as will be hereinafter described, and it is also proved by the fact that the cold tests on oils dewaxed with Pourrex are not lower than oils dewaxed without added Pourrex.

However, the effect of Pourrex on the wax cake is found to be beneficial rather than detrimental. The finger test on the mixture indicates that its sweating properties are not impaired and the comparison of slack wax sweating with and without Pourrex is shown by the following table:

TABLE IV
Sweating plant slack wax—with and without Pourrex

M. P. of slack wax—110°

Stock	Crude scale wax		Drips		Sweating
	Per cent yield	M. P. °F.	Yield	M. P.	Time—Hr.
2.5% Pourrex---	36.4	129	63.6	97.5	77.5
6% Pourrex-----	30.4	130	69.6	96.5	95

A sample of the drips from the sweating of the slack wax containing Pourrex was mixed with completely dewaxed Mid-Continent 60 stock and vacuum distilled until a volume equal to the drips charged had been taken overhead. The maximum still temperature during the distillation was 540° F. under the pressure of 3 mm. Assuming that all of the Pourrex added to the slack wax was in the drips, then all of the Pourrex should be in the bottoms from the vacuum distillation. On that basis the bottoms were added to 180 pale oil to give different concentrations of Pourrex and the cold tests compared with cold tests obtained on the same oil with original Pourrex added. The comparison is shown in the following table:

TABLE V
Recovered Pourrex vs. original Pourrex as cold test depressors for 180 pale

Recovered Pourrex		Original Pourrex	
Percent added	Solid Pt. °F.	Percent added	Solid Pt. °F.
.12	-17	0.1	-14
.58	-25	0.5	-18
1.12	-34	1.0	-36

Thus it is seen that Pourrex does not impair sweating and that it can be completely recovered from the drips by vacuum distillation, or equivalent distillation with steam. The usual practice,

5 however, is to return the drips with incoming oil, and tests have proven that the mixture of incoming oil with about 8% of foots oil (containing Pourrex) can be filtered at rates of about 14 gallons per square foot per hour to give a cake
10 containing about 57% wax which, when dry, has a melting point of 127° F.

It should be understood that instead of effecting all of the refrigeration by vaporizing propane, as hereinabove described, I may cool the mixture
15 by introducing cold propane into warm oil and venting the propane during the addition. I have found, however, that this process cuts down markedly on filter rates and increases the amount of oil in the wax cake. It is more desirable to
20 introduce warm propane and to effect all of the refrigeration by vaporization of propane rather than by heat exchange or the use of sensible heat.

My invention is applicable to the dewaxing of heavy distillates and residual stocks as well as
25 light paraffin distillates, but in this case it is necessary to use larger amounts of propane, and to filter at lower temperatures. When residual stocks are employed I prefer to precipitate the asphalt by means of propane before dewaxing and
30 proceed directly with dewaxing and deasphaltized propane solution. A Mid-Continent residue (298 viscosity at 210° F. Saybolt) deasphaltized with 25% of propane at 65° to 70° F., gives a yield of about 85% deasphaltized oil.
35 When this oil is dewaxed using 70% by volume of propane as a diluent I obtain a wax cake containing 70.3% wax. My invention is also applicable to both treated and untreated wax-bearing oil stocks and, in fact, to any wax-bearing
40 material containing sweatable wax.

With regard to the percent of wax removed from the 136 viscosity at 100° F. pipe still paraffin distillate, a comparison was made between the Pourrex-propane method and the present methods.
45 Assuming a solid point (dewaxed oil) of 30° F. with present methods against 15° F. for the propane-Pourrex method it was found that the wax recovery is approximately 30% greater using the propane-Pourrex method than with the present method.
50

An extremely important feature of my invention is the low operating cost. Estimates in one instance show that the cost per 100 gallons of solution charged will be less than one-third the
55 cost per 100 gallons with present methods. The cost of removing sweatable wax from paraffin distillate is, of course, much less than the cost of obtaining low pour point lubricating oils from viscous overhead lubricating stocks because of
60 the much smaller amount of propane diluent which is required and because of the fact that the dewaxing is effected at considerably higher temperatures.

While I have described the use of propane as a diluent and refrigerant it should be understood that I contemplate the use of any liquefied normally gaseous hydrocarbon, and particularly mixtures of propane with butane, isobutane, propylene, butylene, ethylene, ethane, etc.
70

In addition to these, I may use other diluents and solvents where convenient. Thus I may dilute very viscous oils with hexane or naphtha to facilitate handling in the various steps of the
75 process. I may also add certain other solvents

to the mixture to decrease the solubility of the wax and provide a more complete separation thereof. Acetone, sulfur dioxide, ethyl and methyl ether are examples of such solvents.

I claim:

1. The method of recovering sweatable wax from a wax mixture, which comprises mixing said wax mixture with propane and a crystallization regulator at an elevated temperature and pressure to effect a homogeneous mixture thereof,
10 chilling the mixture by vaporization of propane to effect the solidification of wax which can be readily filtered to give a dense sweatable wax cake, filtering the diluted oil from the wax and crystallization regulator, sweating the wax to remove the foots oil and crystallization regulator therefrom, and returning the crystallization regulator for admixture with further amounts of sweatable wax.
15

2. The method of claim 1 wherein the foots oil containing the crystallization regulator is admixed with further amounts of the mineral oil stock containing sweatable wax.
20

3. The method of claim 1 wherein the crystallization regulator is recovered from the foots oil by distillation.
25

4. The method of claim 1 wherein the crystallization regulator is a condensation product obtained by the reaction of a chlorinated wax with naphthalene brought about by the catalytic action of aluminum chloride.
30

5. The method of claim 1 wherein the wax mixture undergoing treatment is a paraffin distillate having a viscosity of about 136 seconds Saybolt at 100° F.
35

6. The method of obtaining maximum yields of high melting point wax from mineral oil stocks containing wax, which comprises mixing said stocks with propane and a crystallization regulator, chilling the mixture to about 0° F. to effect solidification of wax which, on filtration, will yield a relatively dry wax cake, filtering said mixture to obtain said dry wax cake, sweating said wax cake to remove low melting point waxes, oil and crystallization regulator from the high melting point waxes, and recovering the crystallization regulator for reuse.
40

7. The method of claim 6 wherein the crystallization regulator is a condensation product obtained by the reaction of a chlorinated wax with naphthalene brought about by the catalytic action of aluminum chloride.
50

8. The method of claim 6 wherein the oil stocks containing wax are paraffin distillates having a viscosity at 100° F. of about 136 seconds Saybolt.
55

9. A process for recovering high melting point wax from a mineral oil stock, which comprises mixing said stock with a crystallization regulator and a liquefied normally gaseous hydrocarbon diluent, refrigerating the mixture by vaporization of a portion of said diluent, leaving about 35% to 50% of the diluent admixed with 65% to 50% of the chilled stock, filtering the mixture to separate diluted wax oil from wax cake containing crystallization regulator, removing diluent from the wax cake, sweating the wax cake to separate high melting point wax from low melting point wax and crystallization regulator, and returning the crystallization regulator for reuse.
60

10. The process of claim 9 wherein the mineral oil stock is a paraffin distillate having a viscosity at 100° F. of about 136 seconds Saybolt.
70